

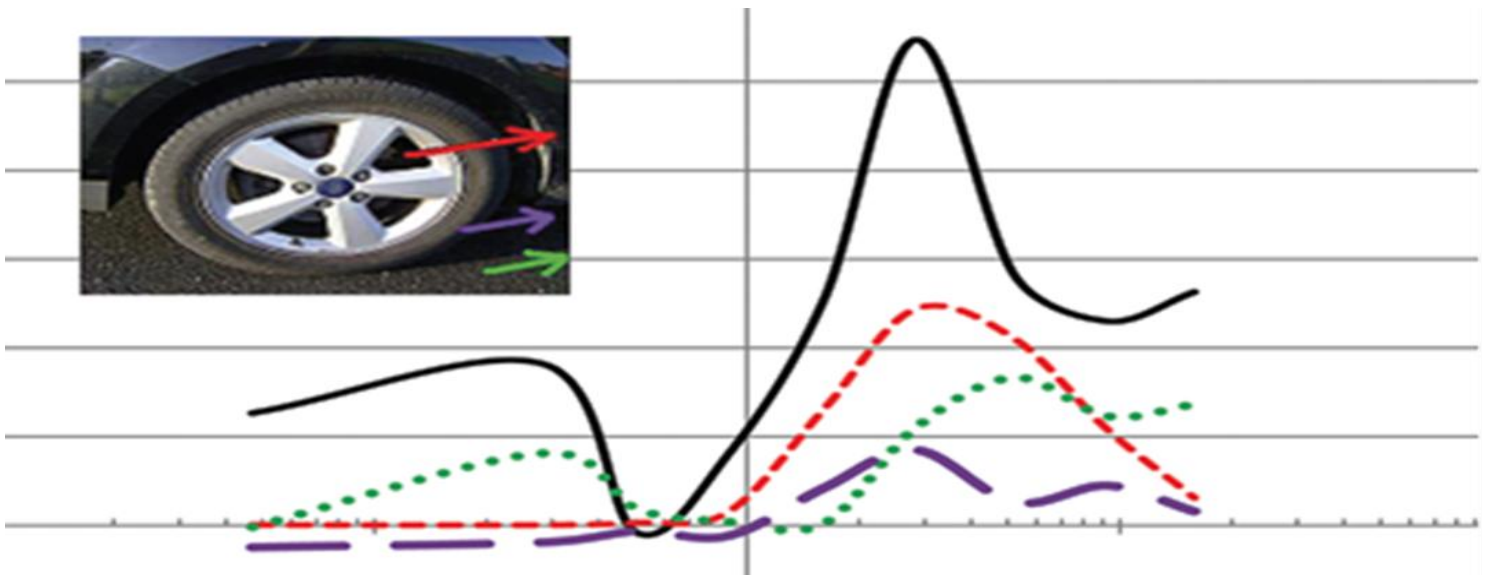
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Non-exhaust traffic related emissions. Brake and tyre wear PM

Literature review

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Abstract

Traffic related sources are a significant contributor of particulate matter, particularly in urban environments and major cities. Traffic related particles can be distinguished into: exhaust traffic related particles, which are emitted as a result of incomplete fuel combustion and lubricant volatilization during the combustion procedure, and non-exhaust traffic related particles, which are either generated from non-exhaust traffic related sources such as brake, tyre, clutch and road surface wear or already exist in the environment as deposited material and become resuspended due to traffic induced turbulence. It is estimated that exhaust and non-exhaust sources contribute almost equally to total traffic-related PM10 emissions. However, as exhaust emissions control become stricter, relative contributions of non-exhaust sources to traffic related emissions will increasingly become more significant. The aim of the present literature review study is to present the state-of-the-art of the different aspects regarding particulate emissions resulting from non-exhaust sources and particularly from brake and tyre wear. For this reason several different literature sources such as peer reviewed papers, research project reports, technical publications, as well as licentiate and doctoral theses were examined and the most significant findings in terms of importance, physicochemical characteristics, EFs and possible adverse health effects are discussed.

CONTENTS

1.	Introduction.....	7
2.	Brake wear.....	9
2.1.	General information – importance	9
2.2.	Mass size distribution.....	12
2.3.	Particle number distribution	15
2.4.	Chemical characterization	17
2.5.	Emission factors.....	20
2.6.	Health relevance	23
3.	Tyre wear.....	25
3.1.	General information – importance	25
3.2.	Mass size distribution.....	29
3.3.	Particle number distribution	34
3.4.	Chemical characterization	37
3.5.	Emission factors.....	39
3.6.	Health relevance	40
4.	Conclusions.....	42
5.	References.....	43

EXECUTIVE SUMMARY

Traffic related sources are a significant contributor of particulate matter, particularly in urban environments and major cities. Traffic related particles can be distinguished into: **exhaust traffic related particles**, which are emitted as a result of incomplete fuel combustion and lubricant volatilization during the combustion procedure, and **non-exhaust traffic related particles**, which are either generated from non-exhaust traffic related sources such as brake, tyre, clutch and road surface wear or already exist in the environment as deposited material and become resuspended due to traffic induced turbulence. It is estimated that exhaust and non-exhaust sources contribute almost equally to total traffic-related PM₁₀ emissions. However, as exhaust emissions control become stricter, relative contributions of non-exhaust sources to traffic related emissions will increasingly become more significant. The aim of the present literature review study is to present the state-of-the-art of the different aspects regarding particulate emissions resulting from non-exhaust sources and particularly from brake and tyre wear. For this reason several different literature sources such as peer reviewed papers, research project reports, technical publications, as well as licentiate and doctoral theses were examined and the most significant findings in terms of importance, physicochemical characteristics, EFs and possible adverse health effects are discussed. Brake wear contributes 16-55% by mass to total non-exhaust traffic related PM₁₀ emissions in urban environments, while in freeways this contribution is significantly lower (~3% by mass) due to lower braking frequency. Somewhat lower contributions (5-30% by mass) have been reported for tyre wear. Most researchers report unimodal mass size distributions of brake wear PM₁₀, with a mass weighed mean diameter of 2-6 µm. On the other hand, tyre wear PM₁₀ often displays a rather bimodal distribution with one peak lying within the fine particle size range and the other within the coarse range (5-9 µm). It is estimated that almost 40-50% by mass of generated brake wear particles and 0.1-10% by mass of tyre wear particles is emitted as PM₁₀. The rest may be attracted by the vehicle or deposit on the road or nearby. Most studies report a bimodal brake wear PM₁₀ number size distribution with one peak lying within the ultrafine mode (<80 nm) and the other within the fine particle mode. On the other hand, the corresponding distributions of tyre wear usually are unimodal. Some researchers find the peak of the PN distribution in the ultrafine mode, while others mention that ultrafine particles are not generated under "normal driving conditions". Regarding the chemical composition of wear particles, brake wear PM₁₀ is characterized by the presence of high concentrations of some heavy metals (Fe, Cu, Zn, Sn, Sb), as well as of S, in both fine and coarse fractions, while noticeable concentrations of organic substances and elemental carbon have been reported in the PM_{2.5} fraction. On the other hand, tyre wear PM₁₀ is characterized by high concentrations of Zn, with Cu and S also displaying high concentrations in both particle fractions. PAHs, benzothiazoles, natural resins, n-alkanes have also been recognized as tyre wear constituents. Both road simulation and receptor modelling studies agree on PM₁₀ brake wear EFs of 2.0-8.8 mg km⁻¹ vehicle⁻¹ and PM₁₀ tyre wear EFs of 3.5-9.0 mg km⁻¹ vehicle⁻¹ for LDVs. Most studies report values of 6-7 mg km⁻¹ vehicle⁻¹ for both sources, which is very close to the corresponding exhaust PM₁₀ EF of modern (Euro 5/6) diesel vehicles. The corresponding EFs of HDVs are estimated to be approximately one order of magnitude higher compared to LDVs. Brake and tyre wear contain particles from all fractions involved in the respiratory function, while some of their chemical constituents have been recognized as dangerous or potentially dangerous. However, there are not comprehensive studies which directly link brake or tyre wear particles with adverse effects on human health. On the other hand, animal and in-vitro studies have reached contradictory conclusions.

ABBREVIATIONS AND ACCRONYMS

ABS	Anti-lock Braking Systems
APS	Aerodynamic Particle Sizer
EC	European Commission
EDX	Energy dispersive X-ray analysis
EEA	Electrical Aerosol Analyzer
EEPS	Engine Exhaust Particle Sizer
EF	Emission Factor
ELPI	Electrical Low-Pressure Impactor
HA	Highly Aromatic oil
HDV	Heavy-Duty Vehicles
ICP-AES	Inductively Coupled Plasma - Atomic Emission Spectrometry
ICP-MS	Inductively Coupled Plasma - Mass spectrometry
LDV	Light-Duty Vehicles
MOUDI	Micro-Orifice Uniform Deposit Impactor
NAO	Non-Asbestos Organic brake pads
NR	Natural Rubber co-polymers
PAHs	Polycyclic Aromatic Hydrocarbons
PBR	Poly-Butadiene Rubber
PCA	Principal Component Analysis
PIXE	Proton Induced X-ray Emission
PM	Particulate Matter
PM _{0.1}	Mass concentration of particles of diameter smaller than 0.1 μm
PM ₁₀	Particles which pass through a size-selective inlet with a 50% efficiency cut-off at 10 μm aerodynamic diameter
PM _{2.5}	Particles which pass through a size-selective inlet with a 50% efficiency cut-off at 2.5 μm aerodynamic diameter
PM _{2.5-10}	Mass concentration of "coarse" particles, determined as the difference between PM _{2.5} and PM ₁₀
PMF	Positive Matrix Factorization
SBR	Styrene-Butadiene Rubber
SEM	Scanning Electron Microscope
SMPS	Scanning Mobility Particle Sizer
TEM	Transmission Electron Microscope
UF	Ultra-Fine particles
WHO	World Health Organization
XRF	X-Ray Fluorescence Analysis

LIST OF TABLES AND FIGURES

Table 1: Review of literature studies regarding the mass size distribution of airborne brake wear particles	13
Table 2: Review of literature studies regarding the particle number distribution of airborne brake wear particles	16
Table 3: Summary of metal concentrations found in brake linings and emitted brake dust	18
Table 4: Most common key tracers used for brake wear particles. Source: [Pant and Harrison, 2013]	20
Table 5: PM ₁₀ emission factors of brake wear reported in the literature for LDVs and passenger cars (mg km ⁻¹ vehicle ⁻¹)	21
Table 6: Literature estimations of the contribution of tyre wear particles to airborne PM (%)	28
Table 7: Review of literature studies regarding the mass size distribution of airborne tyre wear particles	33
Table 8: Review of literature studies regarding the particle number distribution of airborne tyre wear particles	36
Table 9: Most common organic and inorganic key tracers employed for identification of tyre wear particles	38
Table 10: PM ₁₀ emission factors of tyre wear reported in the literature for LDVs and passenger cars (mg km ⁻¹ vehicle ⁻¹)	40
Table 11: Most important chemical constituents of PM ₁₀ wear particles in both fine and coarse particle fraction	43
Figure 1: Disc brake assembly with a single-piston floating caliper and a ventilated rotor	9
Figure 2: SEM images of brake wear particles generated at a road simulation study (left <56 nm, centre <2.5 µm, right <10 µm)	10
Figure 3: An illustration of the contact situation between the pad and disc. A transparent disc is moving from left to right. Some of the wear particles pile up against the contact plateaus and create secondary plateaus. A flow of wear particles in the gap between the pad and disc wear the lowlands of the pad through three-body abrasion	11
Figure 4: Contribution of BW to traffic related PM ₁₀ emissions in Zürich-Weststrasse (right) and Reiden (left) in Switzerland	12
Figure 5: Fractional size contribution for LDV and HDV EFs determined for brake wear related trace elements	13
Figure 6: Schematic representation of the brake dynamometer assembly and measurement instruments used in different studies	14
Figure 7: Particle mass distributions of brake abrasion dust for different types of brake pads	15
Figure 8: Characteristic normalized size distributions of airborne brake wear particles	17
Figure 9: Light and heavy duty vehicle emission factors for Zürich-Weststrasse (street canyon)	22
Figure 10: Particulate matter penetration in human's respiratory system	23
Figure 11: Examples of particles generated by the road simulator and collected after a DMA set at 40 nm. The images were taken with TEM	26
Figure 12: Generalized scheme of particles generated from the interaction of tyre and pavement	27
Figure 13: Simplistic view of tyre composition	28
Figure 14: Particle size distribution determined by volume of particles according to laser diffraction for road particles (A) and tyre wear particles (B)	30
Figure 15: Test room with the rotating axle system in the foreground and the impactor inlets in the back (left) and the VTI road simulator (right)	31
Figure 16: Bimodal mass distributions of particles generated from friction tyres running against different asphalt pavements	32
Figure 17: Unimodal mass distributions of particles generated from friction tyres running against different asphalt pavements	32
Figure 18: Reconstruction of micrometer particle mass through scaling of tracer elements	34
Figure 19: PN size distributions of the aerosol generated at with different tyres on different pavements	35
Figure 20: PN size distributions for road particles (A) and laboratory generated particles (B) as determined by transmission optical microscopy	35
Figure 21: PN size distributions from the EEPS for different maneuvers	36
Figure 22: Analysis of airborne tyre wear particles by means of PIXE	39

1. INTRODUCTION

Particles emitted as a result of road transport activity can be distinguished according to their source into two main categories: **exhaust traffic related particles**, which are a result of incomplete fuel combustion and lubricant volatilization during the combustion procedure, and **non-exhaust traffic related particles**, which are either generated from non-exhaust traffic related sources, or already exist in the environment as deposited material and become resuspended due to traffic induced turbulence. Exhaust traffic related particles have been recognized as a significant contributor to ambient PM and for that reason they have been studied and well characterized in the laboratory under well-defined test conditions. On the other hand, there are a number of non-exhaust processes, involving mechanical abrasion and corrosion, which also result in PM generation and have not been adequately studied. The main abrasion processes leading to the direct emission of particulate matter in the environment are tyre, brake and road surface wear. Other potential sources of direct particle emissions are clutch and engine wear, abrasion of wheel bearings, and corrosion of other vehicle components, street furniture and crash barriers. In addition to direct non-exhaust traffic related emissions, material previously deposited on the road surface can be suspended or resuspended in the atmosphere as a result of tyre shear, vehicle-generated turbulence, and the action of the wind resulting in elevated concentrations of ambient PM.

Several difficulties arise when studying wear particles from non-exhaust traffic related sources. First of all, due to the lack of standard measurement procedures, researchers have employed many different sampling methodologies which often result in non-comparable or even contradictory results and conclusions. Additionally, there are many different parameters which affect wear particles in terms of their physicochemical characteristics and emission rates. For instance, brake wear particles content and emission rates depend on the driving behavior (i.e. frequency and severity of braking), as well as on the conditions under which the braking event occurs (vehicle's speed, ambient temperature and chemicals available in the environment). On the other hand, tyre wear particles generation and composition largely depend on tested tyre characteristics (i.e. size, tread depth, chemical composition, accumulated mileage, set-up), road surface characteristics (i.e. material, porosity, condition) and state of maintenance, vehicle characteristics (i.e. weight, location of driving wheels, engine power), as well as on vehicle's state of operation (i.e. speed, linear acceleration, frequency and extend of braking and cornering). Finally, road dust resuspension depends upon parameters such as traffic density, road surface characteristics and particularly its state of maintenance, local meteorology and vehicle's characteristics and operation (Boulter, 2006).

Depending on their size, wear particles may deposit on the road or very close to it, be partially attracted by the vehicle, or in case of the smaller particles become airborne. It is estimated that approximately 40-50% by mass of generated brake wear particles and only 0.1-10% of tyre wear particles are emitted as PM₁₀ (Garg et al., 2000; Sanders et al., 2003; Mosleh et al., 2004; Wik and Dave, 2009; Kukutschová et al., 2011; Harrison et al., 2012; Kumar et al., 2013). Generally, in the case of road transport, it is commonly assumed that most primary fine particles are emitted from the exhaust, whereas many of the coarse particles are considered to originate from non-exhaust sources. This over-simplifies the situation somewhat; whilst there is a general agreement that exhaust emissions can be classified as PM_{2.5}, there is evidence to suggest that non-exhaust particles contribute to both the fine and coarse modes of PM₁₀ (Boulter, 2006; Dahl et al., 2006; Gustafsson et al., 2008; Kukutschová et al., 2011; Harrison et al., 2012).

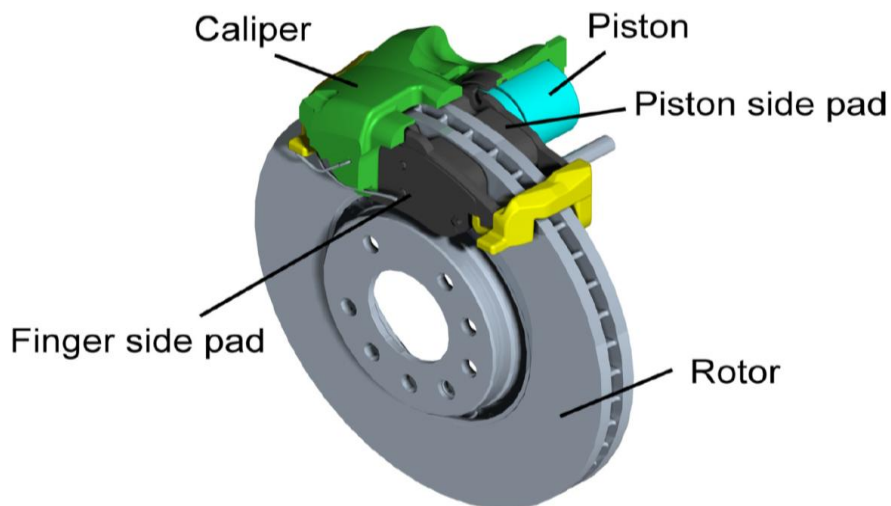
Many researchers report that exhaust and non-exhaust traffic related sources contribute almost equally to total traffic related PM₁₀ emissions, while it is expected that the relative contribution of non-exhaust sources will increase in the forthcoming years (Querol et al., 2004; Bukowiecki et al., 2009a; Amato et al., 2011; Denier Van der Gon et al., 2012). Brake wear contribution to non-exhaust traffic related PM₁₀ emissions is estimated to range between 16-55% by mass, while somewhat lower contributions (5-30% by mass) have been reported for tyre wear. On the other hand, road dust resuspension contributions to non-exhaust traffic related PM₁₀ emissions range between 28-59% by mass. It should be pointed out that significantly lower brake wear contributions (~3% by mass) have been reported in highways due to lower braking frequency, while in case of tyre wear many studies do not adequately distinguish tyre from road surface wear. Regarding the contribution of non-exhaust sources to ambient PM₁₀ concentrations, in case of tyre wear it is estimated to range between 0.8-7% by mass, and depends on various parameters such as the sampling location and methodology, the use of several different chemical markers and the difficulties in distinguishing tyre from road wear particles. This corresponds to ambient PM₁₀ concentrations of 0.2-11 µg m⁻³, while significantly higher contributions have been reported for studded tyres. Road dust resuspension contribution to PM₁₀ ambient concentrations is estimated to range between 1-10 µg m⁻³, with most researchers reporting values of 5-6 µg m⁻³ (Amato et al., 2009; Amato et al., 2010). The aim of the present literature review was to investigate non-exhaust traffic related particles in terms of their importance, physicochemical characteristics, emission factors and possible adverse health effects. Wear particles directly produced on-site by non-exhaust traffic related sources were considered, with emphasis given in brake and tyre wear. Road dust resuspension was not considered at this moment, despite it is a major non-exhaust PM₁₀ contributor, since resuspended particles are not produced on-site but actually already exist as deposited material from different sources. Finally, clutch wear was not considered because the enclosed nature of the clutch mechanism probably means that much of the wear material is retained inside the housing.

2. BRAKE WEAR

2.1 GENERAL INFORMATION - IMPORTANCE

Currently there are two main brake system configurations in use: **disc brakes**, in which flat brake pads (lining materials for disc brakes) are forced against a rotating metal disc, and **drum brakes**, in which curved brake shoes (lining materials for drum brakes) are forced against the inner surface of a rotating cylinder. Passenger vehicles are usually equipped with disc front brakes and either disc or drum rear brakes. Front brakes have to provide approximately 70% of total braking power, and therefore front brake linings have to be replaced more frequently than rear ones. The main difference between disc and drum brakes is that disc brakes are not sealed off from the ambient air. As a result disc brakes operate more effectively in high temperatures due to their tendency to remain cooler and provide superior performance under stressed conditions. Additionally, in wet weather conditions disc brakes tend to dry more efficiently thus maintaining higher braking effectiveness compared to brake drums. Brake pads and brake shoes also differ somewhat in composition due to the different physical demands. The majority of car braking systems consist of frictional pairs made of a disc, a pad and a caliper (Fig. 1). Rotors used in passenger cars are usually made of grey cast iron but in some cases they can be made of composites such as reinforced carbon-carbon or ceramic matrix composites. State-of-the-art calipers are made of aluminum. Figure 1 depicts a disc brake assembly with a single-piston floating caliper and a ventilated rotor (Wahlström, 2009).

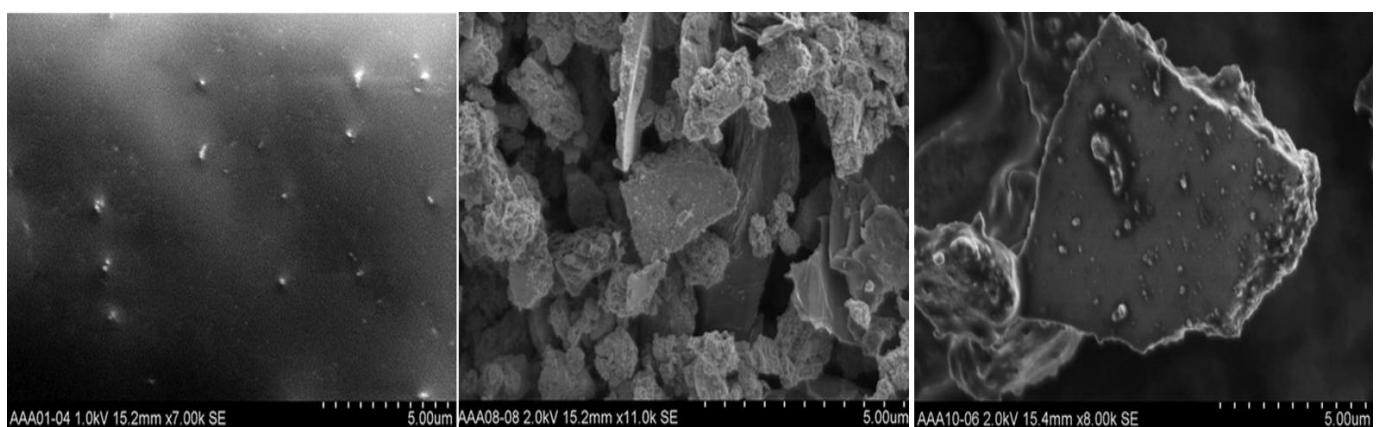
Fig. 1: Disc brake assembly with a single-piston floating caliper and a ventilated rotor.
Source: [Wahlström, 2009]



Brake linings can be made of several different material combinations, but they generally comprise five main components: **binders**, **fibres**, **fillers**, **frictional additives** or **lubricants**, and **abrasives** (Chan and Stachowiak 2004; Thorpe and Harrison, 2008; Wahlström, 2009; Wahlström, 2011; Kukutschová et al., 2011). Binders are used to hold the components of the brake pad together in order to form a thermally stable matrix. A variety of modified phenol-formaldehyde resins are employed as binders. Binders may be modified in a number of ways, depending upon the brake pad specifications. Reinforcing fibers are used in order to provide mechanical strength and structure to the friction lining. They can be classified as metallic, mineral, ceramic or organic, and mainly consist

of copper, steel, brass, potassium titanate, glass, organic material (aramid), and Kevlar (the trademark name of a lightweight synthetic fibre of exceptionally high strength and heat resistance). Fibres usually account for approximately 6-35% (by mass) of the lining matter. Fillers are used in order to reduce cost and improve the brake pad properties (noise reduction, thermal properties improvement). They tend to be low-cost materials such as inorganic compounds (barium and antimony sulphate, magnesium oxides and chromium oxides), silicates (kaolinite clays), ground slag, stone, and metal powders. Lubricants are added to influence the wear characteristics of the lining. Friction modifiers can be inorganic, metallic or organic. Graphite is usually employed as a modifier, but other common materials include ground rubber, metallic particles, carbon black, cashew nut dust, and antimony trisulphide. They usually make up 5-29% by mass of the brake lining. Abrasives are used in order to increase friction, maintain cleanliness between contact surfaces, and limit the build-up of transfer films. They typically account for up to 10% by mass of the lining material. A variety of substances have been employed, including aluminum oxide, iron oxides, quartz and zircon. The proportions of the different components vary according to the type of lining, as well as to the manufacturer (Eriksson et al., 2001; Boulter et al., 2006). For many years brake linings were composed of asbestos fibres, while today brake linings are asbestos free due to serious health concerns (Thorpe and Harrison, 2008). Modern passenger vehicles are usually equipped with three different kinds of brake pads: non-asbestos organic (NAO), semi-metallic, and low metallic. NAO-type brake pads are relatively soft and exhibit low brake noise compared to metallic pads, but they lose braking capacity at high temperature and create more dust than the other types. Low-metallic brake pads are made from an organic formula mixed with small amounts of metals (10-30% by mass), providing them a relatively high abrasive content, which results in high friction and good braking capacity at high temperatures. Semi-metallic brake pads have a high steel fiber and iron powder content which makes them more durable and with excellent heat transfer. On the other hand, they tend to wear down rotors faster, exhibit intrusive noise characteristics, and may not perform as well under low-temperature conditions. The metal content of semi-metallic pads can reach 65% of their total mass. For high performance requirements, or extreme braking conditions (sports cars, ambulances, police cars), metallic linings which contain steel and copper fibres are employed.

Fig. 2: SEM images of brake wear particles generated at a road simulation study (left <56 nm, centre <2.5 μm , right <10 μm). Source: [Kukutschová et al., 2011]



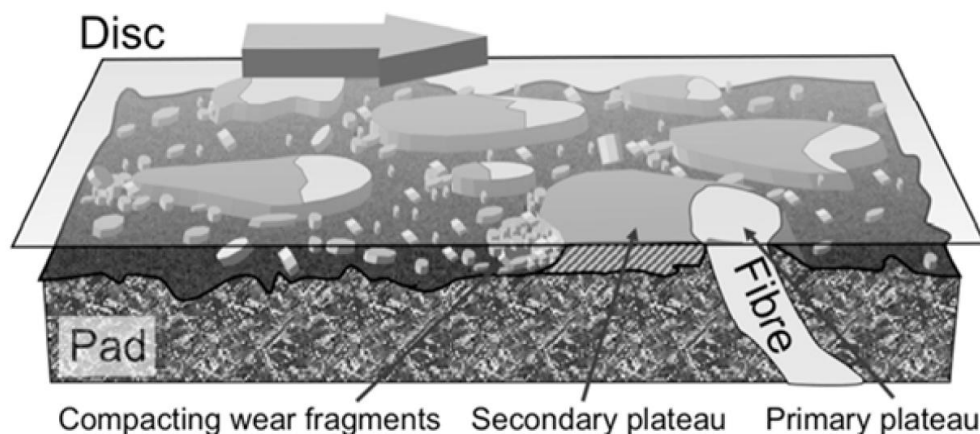
During the braking procedure the caliper acts mechanically on the pad. The pad then slides against the disc and transform vehicle kinetic energy into thermal energy that is dissipated by the air flux. During forced deceleration vehicle brakes become subject to large frictional heat generation, with

subsequent wear of linings and rotors. This procedure generates micron-size particles which are distributed among various sizes (Fig. 2). Furthermore, some disc-brake systems, in order to ensure robust brake performance, require the pads to be in low pressure contact with the rotor. This dragging effectively removes any oxide layer (e.g. rust) from the rotor and keeps the contact surfaces clean. On the other hand, it increases fuel consumption and particle release in the environment (Söderberg et al., 2008).

A detailed explanatory model of the complex contact situation between an organic brake pad and a cast iron disc has been developed and published by some researchers (Ostermeyer, 2001; Österle et al., 2001; Eriksson et al., 2002). In this model the macroscopic friction and wear behavior of a disc brake can be explained by the microscopic contact situation (growth and destruction of contact plateaus) in the boundary layer between the pad and disc (Fig. 3). It has been shown that the plateau surface is covered by a nanocrystalline third body formed by the wear particles and that this third body is mainly made of iron oxides (Österle and Urban, 2006).

Several studies have shown that brake wear debris often differs considerably from the bulk friction material (Österle et al., 2001; Kukutschová et al., 2011). Also, brake wear debris content largely depends on a) the conditions under which braking events occur, with the most important being speed of the vehicle, environmental temperature and chemicals available in the environment (Mosleh et al., 2004; Kukutschová et al., 2011; Olofsson and Olander, 2013) and b) the driving behavior, in particular the frequency and severity of braking events. Considering that brake wear occurs during forced decelerations, the highest concentrations of brake wear particles should be observed near busy junctions, traffic lights, pedestrian crossings, and corners. However, as Kennedy et al. (2002) pointed out, particles may also be released from the brake mechanism or wheel housing some time after the primary emission event.

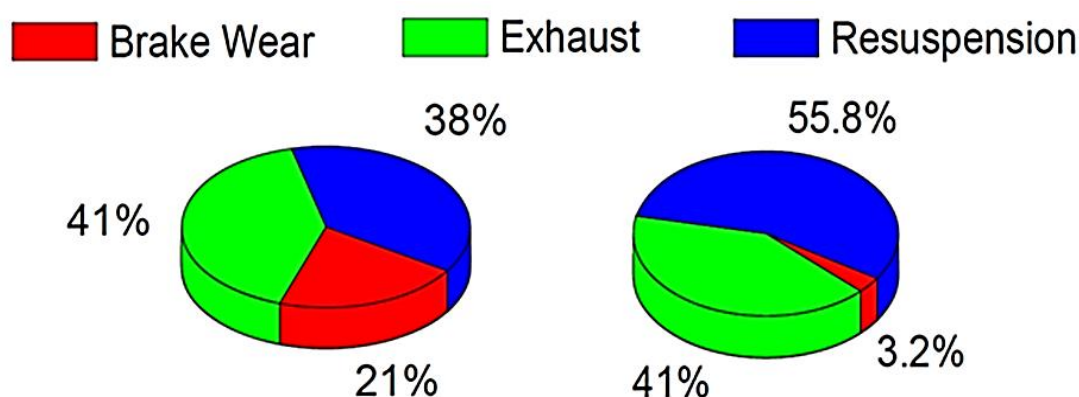
Fig. 3: An illustration of the contact situation between the pad and disc. A transparent disc is moving from left to right. Some of the wear particles pile up against the contact plateaus and create secondary plateaus. A flow of wear particles in the gap between the pad and disc wear the lowlands of the pad through three-body abrasion. Source: [Wahlström, 2011]



Not all brake wear debris becomes airborne. It is estimated that approximately 50% of the generated brake wear particles become airborne (Garg et al., 2000; Sanders et al., 2003; Barlow et al., 2007; Kukutschová et al., 2011) among which 80% is emitted as PM₁₀. The rest may deposit on the (road) surface or be attracted to the vehicle. Braking is considered to be a major source of non-exhaust traffic-related emissions particularly in urban locations. Brake wear is estimated to

contribute approximately 16-55% by mass to non-exhaust traffic-related emissions (Riediker et al., 2008; Bukowiecki et al., 2009a; Gasser et al., 2009; Harrison et al., 2012; Lawrence et al., 2013), while smaller contributions (~3% by mass) have been reported in highways where braking events are less frequent (Abu-Allaban et al., 2003; Bukowiecki et al., 2009a). Figure 4 shows the brake wear contribution to traffic-related emissions in two sampling sites with different characteristics. Taking into consideration that exhaust and non-exhaust sources contribute almost equally to total traffic-related PM emissions (Querol et al., 2004; Bukowiecki et al., 2009a; Amato et al., 2011), as well as the general tendency of decrease of engine exhaust emissions due to the use of catalytic converters, diesel particulate filters (DPF) and improved fuels and engines, it is expected that the relative contribution of brake wear particles to the total PM levels will rise in the forthcoming years (Denier Van der Gon et al., 2012; Denier Van der Gon et al., 2013).

Fig. 4: Contribution of BW to traffic related PM₁₀ emissions in Zürich-Weststrasse (right) and Reiden (left) in Switzerland. Source: [Bukowiecki et al., 2009a]



2.2 MASS DISTRIBUTION

Although brake wear particles are emitted as a result of a predominantly mechanical process and are expected to lie into the coarse size fraction, there are many studies which report high particle concentrations in the fine and ultrafine fractions (Iijima et al., 2007; Riediker et al., 2008; Wahlström et al., 2010b; Kukutschová et al., 2011). Garg et al. (2000) conducted brake dynamometer tests in different brake pads and found that 86% and 63% of the brake wear airborne particle mass was distributed in the PM₁₀ and PM_{2.5} fractions, respectively. They also noticed that a considerable 33% (by mass) of airborne wear particles lied into diameters smaller than 0.1 μm. Sanders et al. (2003) carried out similar laboratory experiments and found that PM₁₀ accounted for 80% of the mass of total brake wear. Iijima et al. (2008) reported that PM_{2.5} accounted for 56–70% of total brake wear mass for three different NAO pads. SEM images show that ultrafine and some of the fine particles seem to be smoother (some of them nearly spherical) and have fewer sharp edges than the coarse particles, thus pointing to thermal and/or chemical generation (Wahlström et al. 2010a). This is probably due to the fact that brake wear process can result in high temperatures at the brake/rotor interface and consequently decompose many of the brake lining materials. Thus it is likely that some materials volatilize during braking and condense in the airstream, contributing to the small particle fraction. The picture is similar for specific elements emitted as a result of the braking procedure. Bukowiecki et al. (2009a) studied the

fractional size distribution of brake wear related trace elements in a street canyon, and found that most of their mass is distributed in the size range larger than 1 μm (LDVs). Some elements (Cu, Mo, Sb) were equally distributed among the fine and coarse particle fraction. On the other hand, most of brake wear particles emitted by HDVs were found in the $\text{PM}_{2.5-10}$ fraction (Fig. 5).

Fig. 5: Fractional size contribution for LDV and HDV EFs determined for brake wear related trace elements. Source: [Bukowiecki et al., 2009a]

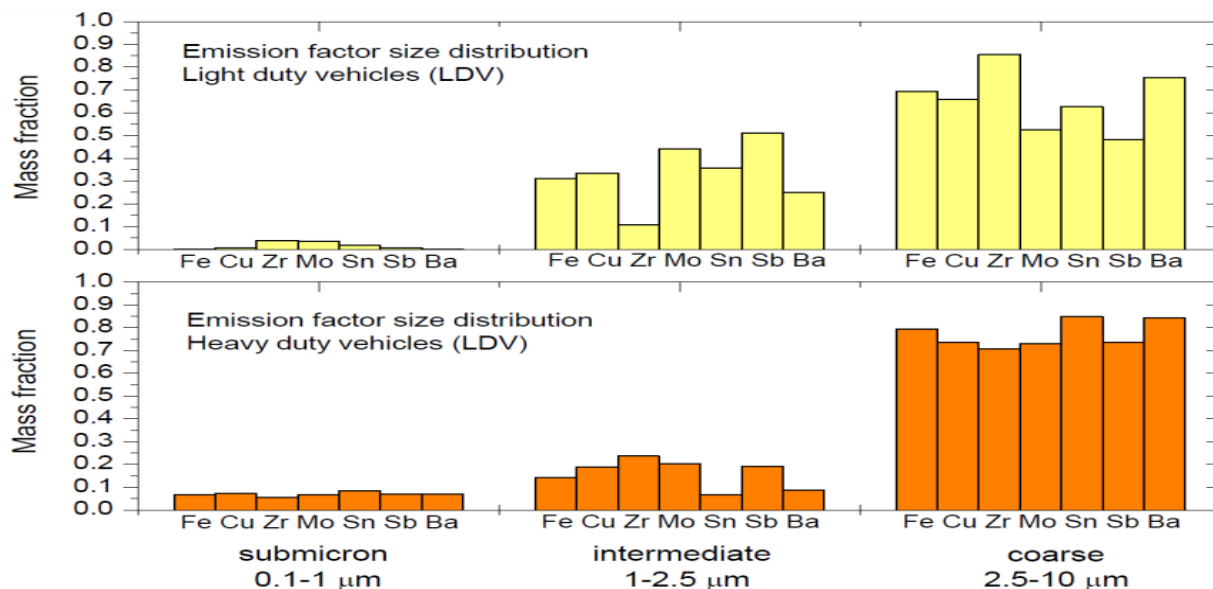
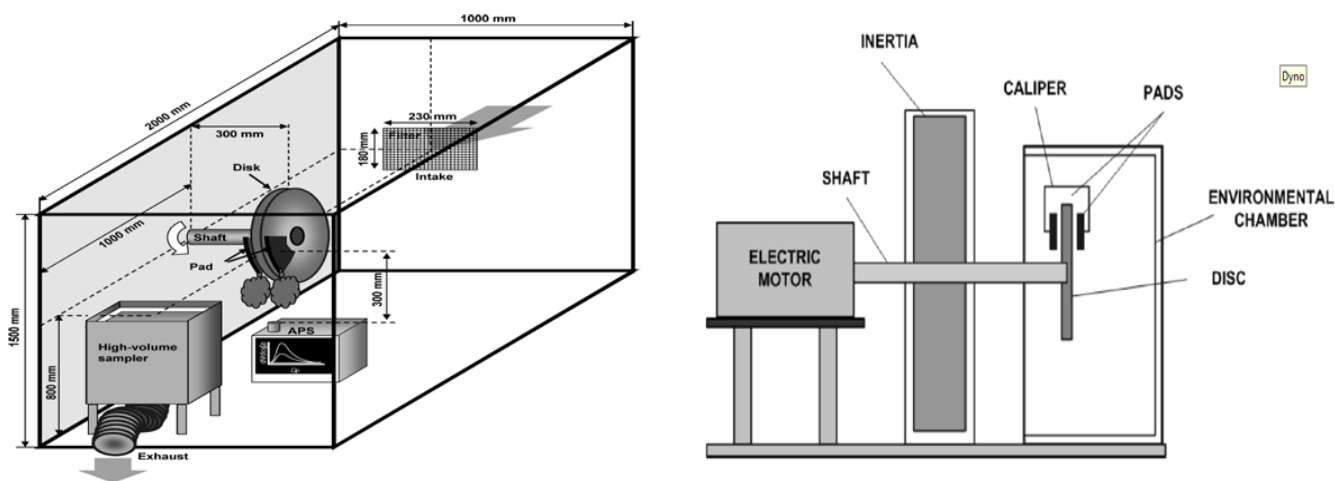


Table 1: Review of literature studies regarding the mass distribution of airborne brake wear particles

Reference	Type of study	Tested	Method	Mass Size Distribution
Garg et al., 2000	Brake dynamometer study	Semi metallic and NAO brake pads	MOUDI (> 0.1 μm)	Unimodal (0.01-1.0 μm)
Sanders et al., 2003	Brake dynamometer study	Low metallic, semi metallic and NAO brake pads	MOUDI - ELPI	Unimodal (4-5 μm)
von Uexküll et al. 2005	Brake dynamometer study	Disc and drum brake pads of trucks	Optical particle counter (> 0.3 μm)	Unimodal (2-3 μm)
Iijima et al. 2007	Brake dynamometer study	NAO brake pads	APS (> 0.5 μm)	Unimodal (3-6 μm)
Iijima et al. 2008	Brake dynamometer study	NAO brake pads	APS (> 0.5 μm)	Unimodal (2.0 μm)
Kukutschová et al. 2011	Brake dynamometer study	Low-metallic brake pads	APS - SMPS - BLPI	Unimodal (2-4 μm)
Harrison et al., 2012	On-road measurement by modelling	Roadside PM attributable to non-exhaust emissions	MOUDI	Unimodal (2-3 μm)

Three kind of studies regarding brake wear particles characterization can be found in the literature: those which investigate particles by means of brake dynamometer test in the laboratory (Garg et al., 2000; Sanders et al., 2003; Mosleh et al., 2004; Iijima et al., 2007; Gasser et al., 2009; Wahlstrom et al., 2010b; Kukutschová et al., 2011), those which perform sampling and analysis of PM in ambient air followed by the use of specific brake wear tracers (Harrison et al., 2012), and those which sample brake wear particles on-road under “real world” driving conditions by means of mobile units (Mathissen et al., 2011). Figure 6 gives a schematic representation of the brake dynamometer assemblies and measurement instruments used in different studies (Iijima et al., 2008; Kukutschová et al., 2011). Table 1 provides an overview of the most important literature studies dealing with the characterization of brake wear particles in terms of their mass size distribution.

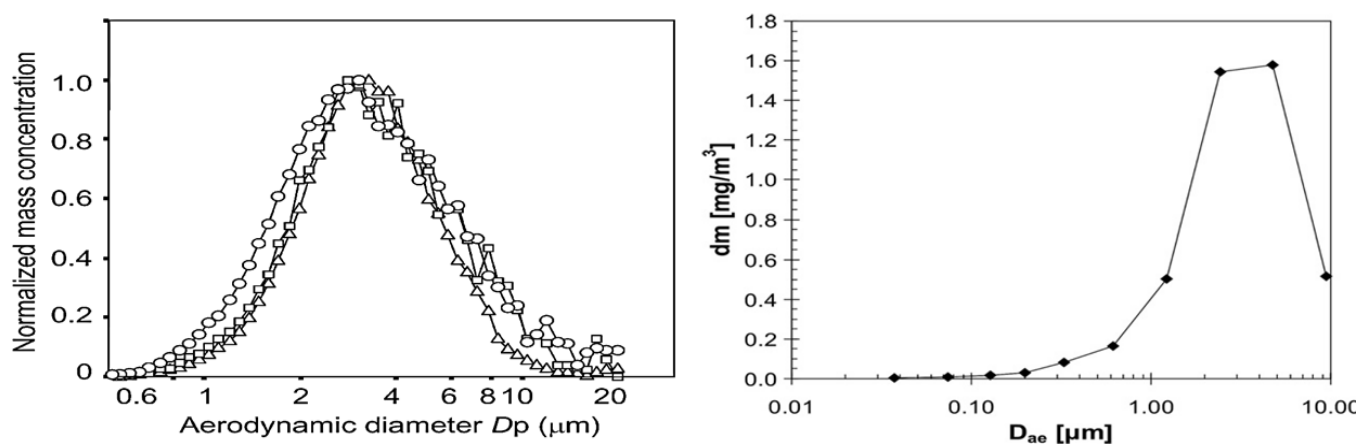
Fig. 6: Schematic representation of the brake dynamometer assembly and measurement instruments used in different studies. Sources: [Left - Iijima et al., 2008; Right - Kukutschová et al., 2011]



Most researchers have reported unimodal brake wear PM_{10} mass distributions with maximum peak ranging between 2-6 μm . Sanders et al. (2003) tested different types of pads under typical urban driving conditions and found a unimodal PM distribution with a mass-weighted mean diameter of 5-6 μm (MOUDI), while Iijima et al. (2007) tested NAO brake pads and reported a unimodal PM_{10} distribution with a mass-weighted mean diameter of 3-6 μm (APS). Both studies were carried out in an open system therefore the particle size distribution could not deviate from the original due to particle aggregation or deposition as a result of the interaction between the particles and the chamber wall. This affect has been described in case of close systems (Iijima et al., 2007). Iijima et al. (2007) also reported that increasing disc temperature results in a slight shift of the mass distribution curve towards higher sizes (Fig. 7 - left). Other studies also revealed unimodal mass distributions with however somewhat lower mass-weighted mean diameter. For instance, Kukutschová et al. (2011) tested low-metallic brake pads and found unimodal distribution with maxima at 2-4 μm (Fig. 7 - right), while von Uexküll et al. (2005) conducted tests on truck brakes (front and rear) and found unimodal mass distributions with peaks at 2-3 μm . On-road measurements have reached similar conclusions to laboratory measurements. For instance, Harrison et al. (2012) collected size-fractionated samples of airborne PM and used the size distribution of specific tracer elements in order to estimate the contribution of brake wear to

particle mass and found that brake wear particles appeared a unimodal PM₁₀ mass distribution with a peak at 2-3 μm (green line).

Fig. 7: Particle mass distributions of brake abrasion dust for different types of brake pads. Source: [Left - Iijima et al., 2007; Right - Kukutschová et al., 2011]



2.3 PARTICLE NUMBER DISTRIBUTION

In order to understand and characterize particles generated from brake wear it is necessary to study their number size distributions. Garg et al. (2000) conducted brake dynamometer tests in different pads and concluded that the highest number of emitted particles lie into diameters smaller than 30 nm, which is the minimum threshold for particle number size detection with the ELPI. This is in agreement with Mathissen et al. (2011) who conducted a road simulation study and investigated the potential generation of ultrafine particles under various real driving conditions by means of an Engine Exhaust Particle Sizer (EEPS). They found that wear particles generated at 100 km h⁻¹ full stop braking events exhibited a bimodal number size distribution with a nucleation mode at 10 nm and a second mode within the ultrafine fraction between 30 nm and 50 nm. They also found that 30 km h⁻¹ full stop braking events led to unimodal size distributions without a separate nucleation mode and slightly shifted towards larger mean particle diameters (70-90 nm). Kukutschová et al. (2011) also investigated the number size distribution of airborne wear particles during a dynamometer test performed in low metallic braking systems. They used both a SMPS and an APS analyzer and found that despite the fact that the generation of small wear particles (<500 nm) at low rotor temperature conditions was negligible, the concentration of nanoparticles smaller than 100 nm significantly increased with the increase of the cast iron disc temperature (up to 340°C). Based on the shape of the distributions and their variation with time they concluded that submicron particles are rather formed by the evaporation/condensation process with subsequent aggregation of primary nanoparticles than by an abrasive type of wear (Fig. 8 – right). Wahlstrom et al. (2010b) also noted a peak in the particle number distribution of brake wear particles generated by low metallic and NAO pads at approximately 100 nm. Additionally, they reported a slight shift of the PN distribution measured by the SMPS towards lower sizes when front brake pads were tested in comparison with rear brake pads. Riediker et al. (2008) tested brake pad materials of six different passenger cars under controlled environmental conditions and found a bimodal particle number distribution with one peak at 80 nm (depending on the tested car and braking behavior), and a second peak at approximately 200-400 nm. They also concluded that full stops

result in higher nanoparticle production compared to normal deceleration. Table 2 summarizes the most important literature studies dealing with the characterization of brake wear particles in terms of their number size distribution.

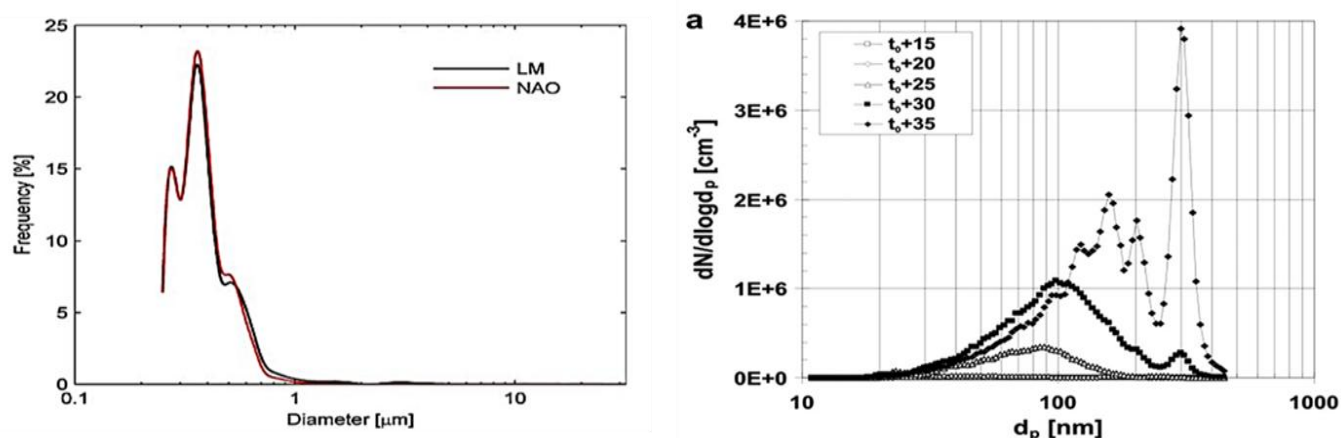
Table 2: Review of literature studies regarding the particle number distribution of airborne brake wear particles

Reference	Type of study	Tested	Method	Particle Number Distribution
Sanders et al., 2003	Brake dynamometer study	Low metallic, semi metallic and NAO brake pads	ELPI	Unimodal (1.0 μm)
Mosleh et al., 2004	Brake dynamometer study	Semi-metallic truck brake pad	Laser Scattering Analyzer	Bimodal (350 nm & 2.0 μm)
von Uexküll et al., 2005	Brake dynamometer study	Disc and drum brake pads of trucks	Optical particle counter (> 0.3 μm)	Unimodal (0.5-1.0 μm)
Iijima et al., 2007	Brake dynamometer study	NAO brake pads	APS (> 0.5 μm)	Unimodal (1.0-2.0 μm)
Riediker et al., 2008	Brake dynamometer study	Different vehicles under full stop and normal deceleration	TEM	Bimodal (80 nm & 400 nm)
Iijima et al., 2008	Brake dynamometer study	NAO brake pads	APS (> 0.5 μm)	Unimodal (0.8-1.0 μm)
Wahlstrom et al., 2010a	Brake dynamometer study	Low metallic and NAO brake pads	GRIMM (>0.25 μm)	Bimodal (280 nm & 350 nm)
Wahlstrom et al., 2010b	Brake dynamometer study	Low metallic and NAO brake pads	GRIMM – SMPS	Multimodal (100, 280, 350, 550 nm)
Mathissen et al., 2011	On-road direct measurement	One vehicle under different conditions	EEPS (<0.56 μm)	Bimodal (10 nm & 40 nm)
Kukutschová et al., 2011	Brake dynamometer study	Low-metallic brake pads	APS – SMPS	Bimodal (100 nm & 300 nm)

Not all studies report peaks in the number size distribution of airborne brake wear particles at the ultrafine fraction. There are several studies which show a peak at approximately 350 nm. For instance, Wahlström et al. (2010a) tested low-metallic and non-asbestos organic braking pads against grey cast iron rotors in a clean air environment, and found by means of a GRIMM aerosol spectrometer a bimodal number size distribution with peaks at approximately 280 nm and 350 nm (Fig. 8 – left). Of course this could be due to instrument's limitation to the size of sampling particles (>0.30 μm). Mosleh et al. (2004) tested a commercial truck semi-metallic braking pad against a grey

cast iron rotor in a pin-on-disc configuration and found a bimodal particle number distribution of brake wear debris with the first peak lying at approximately 350 nm, regardless the testing parameters (sliding speed, nominal contact pressure). They also reported a second peak at higher particle sizes ($\sim 2.0 \mu\text{m}$), which depends on several parameters such as the applied nominal contact pressure and the sliding speed. They concluded that fine wear particles originate from the cast iron disc, whereas coarse particles mainly come from the brake pad material. Wahlström et al. (2010b) used a pin-on-disc tribometer equipped with a GRIMM aerosol spectrometer in order to test airborne wear debris generated from the interaction of non-asbestos organic and low metallic pads with grey cast iron rotors. They reported that low metallic pads result in higher wear rates of the rotor material than the NAO pads, and thus in higher concentrations of airborne wear particles. In all cases similar size distributions with maxima at around 280, 350, and 550 nm were obtained.

Fig. 8: Characteristic normalized size distributions of airborne brake wear particles. Source: [Left - Wahlström et al., 2010a; Right - Kukutschová et al., 2011]



Finally, there are some studies reporting the first peak of the particle size distribution at approximately $1.0 \mu\text{m}$. For instance, Sanders et al. (2003) conducted dynamometer and on-road vehicle tests in three different classes of lining materials and found a maximum peak at approximately $1.0 \mu\text{m}$ (ELPI). Iijima et al. (2007) used an APS spectrometer with high temporal and size resolution in order to measure the number distribution of the brake dust from NAO brake pads and found a peak at approximately $1.0 \mu\text{m}$, with a tendency to shift to coarser sizes with increasing disc temperature. Again this could be due to instrument's limitation to the size of sampling particles ($>0.50 \mu\text{m}$). Based on the number concentration they also demonstrated that approximately 90% of brake abrasion dust is distributed in the fine particles fraction. Overall, brake wear particle number distributions usually appear to be bimodal with both peaks lying within the fine particle mode.

2.4 CHEMICAL CHARACTERIZATION

Although there is not enough evidence available in order to identify the effect of different chemical constituents at the population level, there is evidence for the hazardous nature of some PM constituents such as the black carbon present in $\text{PM}_{2.5}$, as well as specific constituents (i.e. PAHs, metals, inorganic salts) which are attached to black carbon (WHO, 2013). Therefore chemical composition of particles should be taken into account when investigating possible adverse health

effects of PM on humans. Several epidemiology studies have correlated adverse health responses with increased concentrations of carbonaceous species in the PM (Lipfert et al., 2006; Ostro et al., 2006; Kelly and Fussell, 2012), as well as with the presence of trace elements and heavy metals (Pope et al., 2007; Ostro et al., 2007; Kelly and Fussell, 2012).

Although the chemical composition of brake wear debris significantly differs from the chemical composition of the original brake lining material (Österle et al., 2001; Kukutschová et al., 2011), it is necessary to look into both linings and wear debris composition in order to gain a comprehensive view of how the braking process affects the chemical constituents of brake wear particles. The chemical composition of commercial brake lining varies significantly among different types of pads and largely depends upon the manufacturer. Each brand has its own formulation, and detailed chemical composition is not provided by the manufacturer. However, most researchers report Fe, Cu, Zn and Pb to be the most abundant metals present in the brake lining material, with however Pb having been replaced in modern brake linings (Bukowiecki et al., 2009a). Fe is the most abundant metal (up to 60%), with its content varying according to the type of lining (Gadd and Kennedy, 2000; Chan and Stachowiak, 2004; Kukutschová et al., 2011), while Cu and Zn also display high concentrations (Westerlund, 2001; von Uexkull et al., 2005; Iijima et al., 2007). K and Ti are also present in considerable concentrations. Significant Pb content, up to 12% wt. has been reported in older studies (Thorpe and Harrison, 2008), with latest studies showing a remarkable decrease (0.2%, Kukutschová et al., 2011). Other metals such as Ba, Mg, Mn, Ni, Sn, Cd, Cr, Ti, K and Sb have also been found (Boulter, 2006; Thorpe and Harrison, 2008), although in concentrations lower than 0.1% wt. (Kukutschová et al., 2011). Recently, brake wear emissions have been cited as a potentially important source of Sb in the environment, since some brake linings contain 1-5% Sb in the form of stibnite (Sb_2S_3). Sb_2S_3 is employed as a lubricant in order to reduce vibrations and improve friction stability and it can be oxidized to Sb_2O_3 during the braking process. Sb_2O_3 has been categorized as a potentially carcinogenic substance and has been shown to be partially soluble in physiological fluids (Von Uexküll et al., 2005; Varrica et al., 2013).

Table 3: Summary of metal concentrations found in brake linings and emitted brake dust. Source: [Thorpe and Harrison, 2008]

Metal	Car brake linings (mg/kg)	Car brake dust (mg/kg)	Metal	Car brake linings (mg/kg)	Car brake dust (mg/kg)
Al	3765	330-2500	K	857	190-5100
As	<2.0-18	<2.0-11	Mg	6140	83,000
Ba	2638	5900-74,400	Mn	181-3220	620-5640
Ca	14,300	920-8600	Mo	0.4-215	5.0-740
Cd	<1.0-41.4	<0.06-2.6	Na	15,400	80
Co	6.4-45.8	12-42.4	Ni	3.6-660	80-730
Cr	<10-411	135-1320	Pb	1.3-119,000	4.0-1290
Cu	11-234,000	70-39,400	Sb	0.07-201	4.0-16,900
Fe (%)	1.2-63.7	1.1-53.7	Zn	25-188,000	120-27,300

Table 3 provides an overview of most common elements and their concentrations in brake linings and brake dust. Limited information regarding the presence of specific organic compounds is available in the literature. Brake linings have to withstand excessive mechanical and heat stress,

therefore their organic content is of high resistance to thermal and mechanical stress. Also an organic content of high resistance to solvents is required since they have to be refractory to attack by solvents in case of brake fluid leakages. Gadd and Kennedy (2000) examined 6 different commercial brake pads and reported phenolic compounds to be the most abundant species present in the brake pad extracts. Other compounds detected included carbonyl compounds, organic acids, methyl-esters and aromatic carboxylic acids all in trace concentrations.

Chemical properties of the parent lining material are often modified due to high temperatures and pressures reached during the braking process. Not all particles emitted from brake wear become airborne. Several researchers have reported that brake wear is characterized by a specific pattern of some heavy metals (Fe, Cu, Zn, Zr, Sn, Sb) in the airborne PM concentrations (Boulter, 2006; Bukowiecki et al., 2009a). As seen in Table 4, many researchers have used these elements as specific tracers for brake wear (Pant and Harrison, 2013). Wahlström et al. (2010a) tested low-metallic and NAO braking pads and found that emitted fine particles mainly comprised Fe, Cu, Ti, Al, as well as oxygen and carbonaceous species. On the other hand, most of the coarse particles appeared as flakes and mainly consisted of Fe in the form of its oxides. They concluded that these particles were mechanically generated suggesting disc wear. Some of the coarse particles also contained Ti, Cu, and Al and were attributed to the brake pads. Kukutschová et al. (2011) tested low metallic brake pads and reported that the finest brake wear PM fraction was dominated by metallic and carbonaceous species. PIXE analysis revealed that Fe dominated metallic content in both fine and coarse fractions, while TEM analysis showed the presence of maghemite ($\gamma\text{-Fe}_2\text{O}_3$), magnetite ($\text{FeO-Fe}_2\text{O}_3$), and amorphous carbon in the nanoparticle fraction, and $\gamma\text{-Fe}_2\text{O}_3$, $\text{FeO-Fe}_2\text{O}_3$, and hematite ($\alpha\text{-Fe}_2\text{O}_3$) in the fine fraction. PIXE analysis also revealed the presence of Cu, Sn and Zn in various oxides form, as well as of S in relatively high concentrations in all measured fractions. Fe domination among trace elements was attributed to the easiest fragmentation of Cu, Zn, and Sn due to their lower mechanical properties, as well as their lower melting points, compared to steel and cast iron. Regarding carbonaceous species, Raman microspectroscopy showed the presence of carbon black, which was attributed to the oxidative wear and subsequent deposition from related volatiles (Yu et al., 2009), as well as of graphitic particles emitted as a result of abrasive wear. Similarly, Gasser et al. (2009) examined heavy metals and carbonaceous species in freshly emitted brake wear particles from six different vehicles and found high concentrations of Fe, Cu and OC, in both “normal deceleration” and “full stop” braking patterns. Fe, Cu and Mn significantly correlated between each other suggesting their common brake wear origin. They also found that OC was present in higher concentrations (one order of magnitude) compared to elemental carbon (Riediker et al., 2008). Garg et al. (2000) conducted brake dynamometer tests in seven different brake pads and found average trace elements percent in total PM_{10} mass of 72%. Fe, Cu, Ti, S and Zr were the most abundant species, while total carbon accounted for 17-21% of the airborne PM_{10} mass. Over 96% of the total carbon mass was attributed to organic substances in agreement with Riediker et al. (2008). On the other hand, PIXE analysis in brake dust samples revealed lower concentrations of trace elements compared to airborne PM, probably due to higher volatilization of organic constituents compared to dust samples in airborne PM. Similar results were also reported by Sanders et al. (2003). Regarding the presence of Sb in airborne PM existing studies are rather contradictory. Some researchers reported the absence of Sb in airborne wear particles (Wahlström et al., 2010a; Kukutschová et al., 2011), which is supported by the intention of brake manufacture companies to substitute Sb in modern brake linings (von-Uexküll et al., 2005). On the other hand, Varrica et al. (2013) undertook a detailed study on Sb in brake pads residue, road dust, and atmospheric PM samples and concluded that Sb is present in road dust and atmospheric PM

samples in the form of Sb (III) and Sb (V). They also found that brake linings contain Sb_2O_3 and Sb_2S_3 . Sb_2S_3 was also detected in some of the ambient PM_{10} samples despite the fact that it is easily decomposed into more stable compounds during the brake abrasion process. Regarding specific organic compounds there is still a lack of information. A study conducted by Rogge et al. (1993) revealed that only a small fraction of the organic content of brake dust could be extracted and analyzed by conventional laboratory techniques. Among the organic compounds detected, polyalkylene glycol ethers (56.9%) and n-alkanoic acids (34.3%) were the most abundant species, while n-alkanes, PAHs and substituted PAHs were also detected in trace concentrations. In conclusion, although the presence of species like transition metals and carbonaceous compounds in wear particles is confirmed, there is still little information about specific constituents of brake wear PM_{10} and particularly about their organic fraction.

Table 4: Most common key tracers used for brake wear particles. Source: [Pant and Harrison, 2013]

Reference	Tracer	Reference	Tracer
Adachi et al., 2004	Fe, Ba, Cu, Sb, Zr	Bukowiecki et al., 2009a	Fe, Cu, Zn, Zr, Mo, Sn, Sb
Schauer et al., 2006	Fe, Cu, Ba	Amato et al., 2011	Fe, Cu, Zn, Cr, Sn, Sb
Tanner et al., 2008	Cu, Cd	Apeagyei et al., 2011	Fe, Ti, Cu, Ba
Harrison, 2009	Ba, Cu	Duong and Lee, 2011	Ni, Cu
Dongarra et al., 2009	Cu, Mo, Sb	Song and Gao, 2011	Sb, Cu, Fe, Pb
Keuken et al., 2010	Cu	Harrison et al., 2012	Ba, Cu, Fe, Sb

2.5 EMISSION FACTORS

Emission factors (EFs) are used by researchers and regulating agencies as a tool to quantify the emission of a specified pollutant by an individual vehicle or a vehicle fleet mixture. They are functional relations that predict the quantity of a pollutant that is emitted per distance driven, energy consumed, or amount of fuel used. EFs are typically derived for vehicle categories and depend on many parameters such as vehicle characteristics, vehicle emission control technologies, type and quality of fuel used, as well as the ambient and operating conditions (Franco et al., 2013). In order to determine EFs from non-exhaust sources, and therefore their contributions to atmospheric particle concentration, either direct measurement from the sources is employed, including real world test conditions and/or laboratory experiments, or receptor modeling is applied. Although, direct measurements provide EFs of a relatively small number of vehicles, they have the advantage of being conducted under very well controlled conditions. However, in case of brake wear there is a difficulty in simulating real-life braking conditions under controlled tests. On the other hand, receptor modeling requires accurate knowledge of source composition and assumes that the sources specified are responsible for the species measured at the receptor (Barlow et al., 2007). A list of key tracers used by various researchers over the last decade for identifying brake wear is presented in Table 4. Sternbeck et al. (2002) also proposed the ratio of Cu:Sb (4.6 ± 2.3) as characteristic of brake wear particles but differences often appear in the literature due to variations in brake pad composition and site characteristics, as well as

contributions of these particular metals from other sources (Adachi and Tainosho, 2004; Hjortenkrans et al., 2007; Pant and Harrison, 2013).

Garg et al. (2000) conducted brake dynamometer tests in commercial brake pads used in light duty vehicles and found PM_{10} , $PM_{2.5}$, and $PM_{0.1}$ brake wear EFs of 2.9-7.5, 2.1-5.5 and 1.2-3.1 $mg\ km^{-1}\ vehicle^{-1}$, respectively. The upper limit of the range for PM_{10} EFs was very close to the U.S. EPA value of 7.9 $mg\ km^{-1}\ vehicle^{-1}$ which was calculated for light-duty petrol vehicles equipped mainly with asbestos brakes (Boulter, 2006). Sanders et al. (2003) also reported a relatively high brake wear PM_{10} EF in tests conducted with low metallic, semi metallic and NAO brake pads (Table 5). Somewhat lower PM_{10} EFs (1.8-4.9 and 3.5 $mg\ km^{-1}\ vehicle^{-1}$ for LDVs and HDVs, respectively) were reported by Lükewille et al. (2001), while Iijima et al. (2008) calculated PM_{10} EFs of 5.8 $mg\ km^{-1}\ vehicle^{-1}$ and $PM_{2.5}$ EFs of 3.9 $mg\ km^{-1}\ vehicle^{-1}$ in a study conducted with NAO brake pads. Overall, it is concluded that brake wear EFs for LDVs deriving from direct measurements fall in the range of 2.0-8.0 $mg\ km^{-1}\ vehicle^{-1}$ (PM_{10}) and 2.1-5.5 $mg\ km^{-1}\ vehicle^{-1}$ ($PM_{2.5}$).

Table 5: PM_{10} emission factors of brake wear reported in the literature for LDVs and passenger cars ($mg\ km^{-1}\ vehicle^{-1}$)

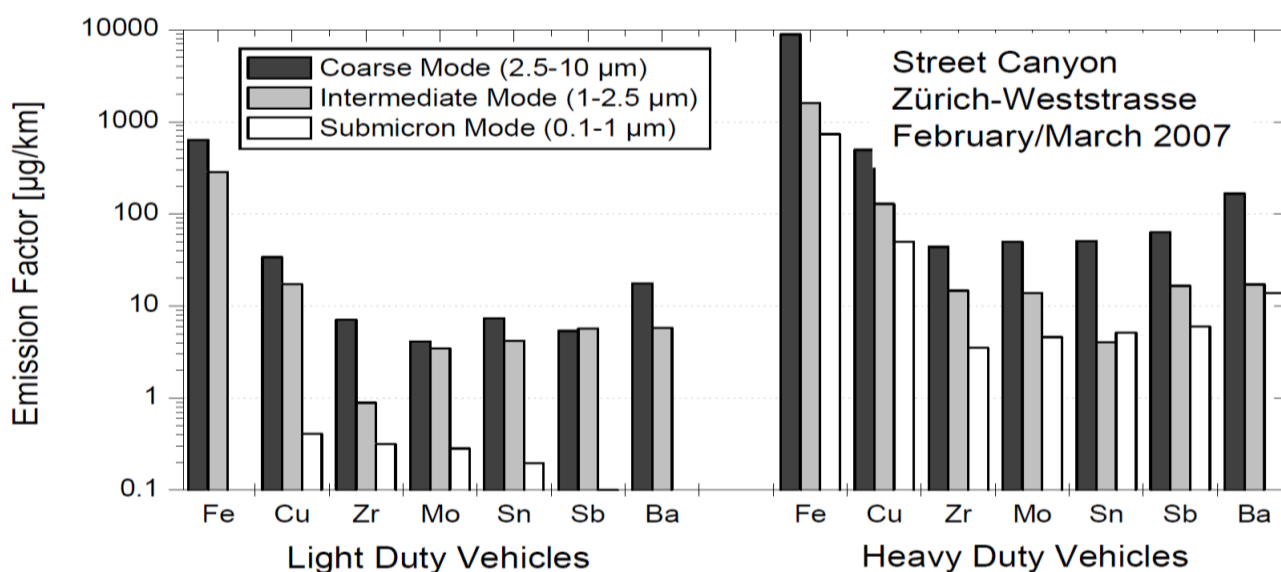
Reference	Type of study	PM_{10} EF
USEPA, 1995	Emissions Inventory	7.9
Garg et al., 2000	Brake dynamometer study	2.9-7.5
Lükewille et al., 2001	Emissions Inventory	1.8-4.9
Sanders et al., 2003	Brake dynamometer study	8.1
Luhana et al., 2004	Receptor modelling	8.8
Barlow et al., 2007	Emissions Inventory	4.0-8.0
Iijima et al., 2008	Brake dynamometer study	5.8
Bukowiecki et al., 2009a	Receptor modelling	8.0
NAEI, 2012	Emissions Inventory	7.0
AVERAGE VALUE		6.7

Abu-Allaban et al. (2003) employed chemical mass balance receptor modeling and SEM techniques in order to determine brake wear EFs of light and heavy duty vehicles at roadside locations in the U.S.A. They found PM_{10} EFs of 0-80 $mg\ km^{-1}\ vehicle^{-1}$ for LDVs and 0-610 $mg\ km^{-1}\ vehicle^{-1}$ for HDVs. The corresponding $PM_{2.5}$ EFs were 0-5 and 0-15 $mg\ km^{-1}\ vehicle^{-1}$. In general, high brake wear EFs were observed at freeway exit sites, while brake wear emissions in highways and tunnels were negligible. Rauterberg-Wulff (1999) also reported very low PM_{10} brake wear EFs in tunnel studies, namely 1.0 $mg\ km^{-1}\ vehicle^{-1}$ for LDVs and 24.5 $mg\ km^{-1}\ vehicle^{-1}$ for HGVs. PMF was employed during the APART project, in order to perform the mathematical identification of the abrasion sources from the experimental data obtained by two different locations in Switzerland. The results in this case better comply with the ones from direct measurements. More specifically, PM_{10} brake wear EFs in Zürich-Weststrasse (urban street canyon) were found to be $8.0\pm 4.0\ mg\ km^{-1}\ vehicle^{-1}$ (LDVs) and $81\pm 39\ mg\ km^{-1}\ vehicle^{-1}$ (HDVs). EFs in a highway sampling location (Reiden) turned out to be significantly lower, displaying values of 1.6 ± 1.1 and $9.0\pm 7.0\ mg\ km^{-1}\ vehicle^{-1}$ for LDVs and HDVs, respectively. PCA was employed during the PARTICULATES project and a mean

brake wear factor of $8.8 \text{ mg km}^{-1} \text{ vehicle}^{-1}$ was derived in case of passenger vehicles (Luhana et al., 2004). Barlow et al. (2007) reported total brake wear factors of $10\text{-}20 \text{ mg km}^{-1} \text{ vehicle}^{-1}$ (LDVs) and $50\text{-}80 \text{ mg km}^{-1} \text{ vehicle}^{-1}$ (HDVs), with however 40% of these becoming airborne (PM_{10}). This corresponds to PM_{10} EFs of $4\text{-}8 \text{ mg km}^{-1} \text{ vehicle}^{-1}$ for LDVs and $20\text{-}32 \text{ mg km}^{-1} \text{ vehicle}^{-1}$ for HDVs. NAEI provided more generalized exhaust and non-exhaust EFs by combining hot exhaust, cold start and evaporative emissions for each main vehicle type in the UK fleet averaged overall all road types. They calculated a PM_{10} brake wear EF of $7.0 \text{ mg km}^{-1} \text{ vehicle}^{-1}$ (passenger cars), while for $\text{PM}_{2.5}$ the corresponding value was $3.0 \text{ mg km}^{-1} \text{ vehicle}^{-1}$. Additionally, for LGVs they found EFs of $11 \text{ mg km}^{-1} \text{ vehicle}^{-1}$ (PM_{10}) and $4.0 \text{ mg km}^{-1} \text{ vehicle}^{-1}$ ($\text{PM}_{2.5}$) (NAEI, 2012).

Apart from PM EFs there have been several studies reporting EFs for specific constituents of brake wear particles. Garg et al. (2000) found S, Ti, Fe, Cu and Zr emission rates of 0.14, 0.39, 1.37, 0.43 and 0.07 mg km^{-1} , respectively. Bukowiecki et al. (2009a) concluded that both at urban street canyon and highway sites, brake wear was characterized by a characteristic pattern of Fe, Cu, Zn, Mo, Zr, Sn, Sb and Ba. As shown in Figure 9 the highest EFs were found for Fe and Cu both for LDVs and HDVs. Ba, Zr, Mo, Sn and Sb were also found in considerable concentrations but displayed significant lower EFs. Pb PM_{10} EFs were lower when compared to older studies, indicating that Pb in brake linings has largely been replaced by other elements. Wahlin et al. (2006) used the Constrained Physical Receptor Model in order to analyze the data received during a sampling campaign conducted in Copenhagen and found a brake wear related Cu PM_{10} EF of $0.7 \pm 0.2 \text{ mg km}^{-1} \text{ vehicle}^{-1}$. Bukowiecki et al. (2009b) used the dataset derived from the APART project and determined brake wear related Sb PM_{10} EFs of 11 ± 7 and $86 \pm 42 \text{ } \mu\text{g km}^{-1} \text{ vehicle}^{-1}$ for LDVs and HDVs, respectively. They also found that Sb was distributed in coarse, fine and ultrafine particle fractions. Sternbeck et al. (2002) reported similar Sb EFs in a study conducted in two heavily trafficked tunnels in Gothenburg. They found Sb PM_{10} EFs of 32 and $51 \text{ } \mu\text{g km}^{-1}$ and attributed the majority of emitted Sb in brake wear. They also reported PM_{10} Cu EFs of 0.17 and 0.15 mg km^{-1} . In summary, brake wear is responsible for relatively high Fe (up to $1 \text{ mg km}^{-1} \text{ vehicle}^{-1}$ for LDVs), and Cu emissions ($0.05\text{-}0.7 \text{ mg km}^{-1} \text{ vehicle}^{-1}$ for LDVs). Sb displays EFs of $11\text{-}51 \text{ } \mu\text{g km}^{-1} \text{ vehicle}^{-1}$.

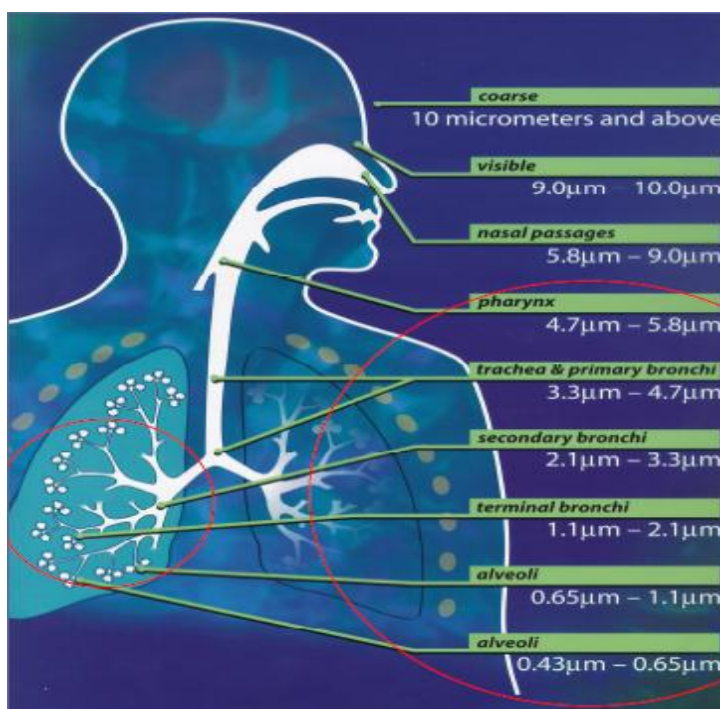
Fig. 9: Light and heavy duty vehicle emission factors for Zürich-Weststrasse (street canyon). Source: [Bukowiecki et al., 2009a]



2.6 HEALTH RELEVANCE

Several important key factors need to be taken into account in order to investigate wear particles' toxicity and their potential adverse effects on human health, with the most important being their size distribution, agglomeration state, chemical composition, surface area, as well as their chemistry and surface charge (Oberdörster et al., 2005). There are many studies demonstrating that particle size is an important factor affecting particles deposition in the respiratory tract (Samet et al., 2000; Pope et al., 2002; Kumar et al., 2013). The World Health Organization reported that adverse health effects of inhalable PM are due to exposure over both short (hours, days) and long (months, years) terms and include: respiratory and cardiovascular morbidity, (aggravation of asthma, respiratory symptoms, increase in hospital admissions), as well as mortality from cardiovascular and respiratory diseases and from lung cancer (WHO, 2013). While coarse particles are mainly deposited in the upper respiratory tract (nose and throat), ultrafine particles penetrate deep into the lungs (Fig. 10). Since they penetrate deep into the respiratory tract, they pose hazards related to oxidative stress and inflammation (Balakrishna et al., 2009), as a result of their increased surface area and the higher reactivity of the produced free radicals (Oberdörster et al., 2005; Karlsson et al., 2005). They can also enhance early atherosclerosis, partly due to their high content in redox chemicals and their ability to synergize with known proatherogenic mediators in the promotion of tissue oxidative stress (Araujo and Nel, 2009). Several studies have shown that ultrafine particles may become blood-borne and then translocate to other tissues such as the liver, kidneys, and brain (Geiser and Kreyling, 1999; Oberdörster et al., 2005), while experiments to animals have shown translocation of inhaled ultrafine particles containing Mn^{2+} , Cd^{2+} , Ni^{2+} , Hg^{2+} and Al^{3+} to the brain (Tjalve and Henriksson, 1999). As mentioned previously, a considerable fraction of brake wear particles lie into diameters smaller than 100 nm (Garg et al., 2000; Mathissen et al., 2011; Kukutschová et al., 2011), thus posing concerns regarding its potential adverse health effects. However, there are still no comprehensive studies directly linking brake wear PM with adverse health effects on humans.

Fig. 10: Particulate matter penetration in human's respiratory system. Source: [Poepping et al., 2010]



Chemical composition of PM has also been associated with potential adverse effects on human health. Despite that there is no sufficient information regarding the effects of particles' constituents on human health, there are several components of PM (particularly PM_{2.5}) attached to black carbon which have been currently seen as responsible for adverse impacts, with the most important being PAHs, metals and inorganic salts (WHO, 2013). Metallic components, particularly within the fine particle fraction, are very likely to exert adverse health effects. Interest is targeted on transition metals such as Fe, Cu, Ni and Cr due to their potential to produce reactive oxygen species (ROS), and therefore oxidative stress in biological tissues. Oxidative stress occurs when antioxidant systems are overwhelmed by oxidative processes. Oxidative stress can also result from redox cycling by semi-quinone radicals from organic compounds adsorbed on the particles, and from ROS produced by activated macrophages (Karlsson et al., 2005). Metals such as Zn, Al and Pb can also influence the toxic effects of transition metals either by enhancing or by lessening their activity (Kelly and Fussell, 2012). Since brake wear emissions are characterized by high Fe and Cu concentrations it is clear that they should be seriously considered even though currently available data do not yet allow quantification of specific health impacts on the population (Denier van der Gon et al., 2012).

Apart from oxidative stress, heavy metals are considered to be responsible for various other negative responses. Epidemiology studies revealed a high correlation between blood Pb and cardiovascular mortality and morbidity (Schober et al., 2006), while Cu and S have been associated with increased monthly mortality (Pope et al., 2007). Burnett et al. (2000) reported a significant association of Fe, Ni and Zn in the fine particle fraction with short-term mortality. They also found that the total effect of these components was greater than that for fine mass alone, suggesting that the characteristics of the complex chemical mixture in the fine fraction may be a better predictor of mortality than mass alone. Ostro et al. (2007) linked fine particle Ca, Cu, Fe, Zn, Mn, Pb, Ti and V with daily mortality, while Hirshon et al. (2008) associated previous day fine particle Zn concentrations with increased paediatric asthma cases. Toxicology studies in healthy volunteers have associated neutrophilic inflammation in the lungs with Fe and Se, while increased blood fibrinogen levels were connected with high Cu and Zn concentrations (Ghio et al., 2000; Huang et al., 2003). Fe particle agglomerates have been linked to inflammatory responses, decreased transferrin concentrations and increased concentrations of ferritin and lactoferrin in the blood (Ghio et al., 1998). Pulmonary injury and inflammation were connected to high concentrations of Fe, Cu, Ni, Pd and Zn (Ghio et al., 2004), while Schaumann et al. (2004) reported a higher inflammatory effect in the lungs of healthy volunteers following metal-rich particle (high levels of Zn, Cu, Ni and Ca) instillation compared with fractions with a lower metal content (Kelly and Fussell, 2012). There are numerous studies reporting high concentrations of most of these metals in airborne brake wear particles (Pant and Harisson, 2013; Kukutschová et al., 2011; Gietl et al., 2010; Wahlström et al., 2009; Gasser et al., 2009; Hjortenkrans et al., 2007; Sanders et al., 2003; Garg et al., 2000), therefore the possibility that such particles induce adverse health impacts to humans should not be excluded.

Besides general studies there are others which have focused on potential adverse effects of brake wear particles. For instance, toxic effects of brake wear particles in lung cells were investigated *in vitro* by Gasser et al. (2009) who employed a system which enables the exposing of cells directly to freshly emitted brake wear particles. Their results suggest that the metallic content of brake wear particles, and specifically Fe, Cu and Mn, damage tight junctions both in "normal deceleration" and "full stop" braking pattern, probably through a mechanism involving oxidative stress. Brake wear

particles derived from “full stop” braking also found to increase the release of the pro-inflammatory mediator interleukin-8 (IL-8), and therefore pro-inflammatory responses in lung cells, probably through a mechanism involving organic compounds and black carbon, rather than oxidative stress. This observation is enhanced by the study of Mazzarella et al. (2007) who also found a significant correlation between increased pro-inflammatory responses and high concentrations of carbon in the small particles size range. Riediker et al. (2004) linked adverse health responses to a particle source with a brake wear signature. They reported that fine particles originating from speed-changing traffic modulates the autonomic control of the heart rhythm, increases the frequency of premature supraventricular beats and elicits pro-inflammatory and pro-thrombotic responses in young (23-30), healthy, non-smoking men. They proposed that these health effects might be associated with the levels of Cu, which strongly increased under speed-changing traffic conditions and was associated with brake abrasion. Besides brake wear, these responses were also linked to emissions from accelerating vehicles and diesel combustion products. Additionally, the researchers pointed out that long-term cardiovascular risk cannot be excluded, especially when considering the reported increase in myocardial infarction among professional drivers, and the increase in mortality among people living near major roadways.

Several studies have reported PM_{2.5} enriched with airborne Sb compared to crustal materials in urban areas (Bukowiecki et al., 2009a; Iijima et al., 2007). Additionally, composition analysis of fine particles in urban areas has revealed highest concentrations of Sb in the majority of edgy-shaped particles, compared to spherical and cotton-like particles (Iijima et al., 2007; Furuta et al., 2005). This observation suggests that such particles are most likely generated by the mechanical abrasion of Sb-enriched materials, with the most probable being brake pads containing Sb₂S₃ (i.e. non-asbestos organic pads). During braking events, brake pads may reach temperatures high enough to induce oxidation of Sb₂S₃ to Sb₂O₃, which has been classified as a possible human lung carcinogen by the International Agency for Research on Cancer (IARC, 1989; Varrica et al., 2013) and as a “Class 3 Carcinogen” via dust inhalation according to 67/548/EC and amendments.

Besides the chemical composition and the size distribution, the toxicity of brake wear particles also depend on other properties such as their surface chemistry and area per mass, as well as their surface charging. In case of nanoparticles the greater surface area per mass compared with larger-sized particles of the same chemistry may render them biologically more active. This activity includes a potential for inflammatory and pro-oxidant, but also antioxidant activity (Oberdörster et al., 2005). This could also be the case for brake wear nanoparticles. Thus, the potential toxicity of these particles has to be examined in terms of these properties, too.

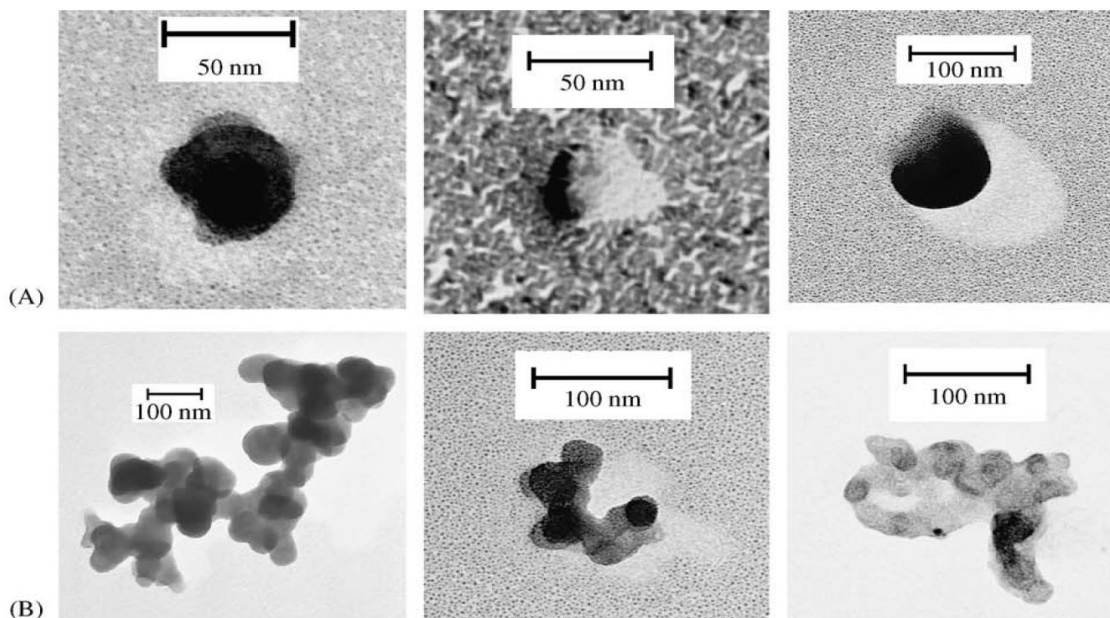
3. TYRE WEAR

3.1 GENERAL INFORMATION - IMPORTANCE

Tyre wear particles are generated either by shear forces between the tread and the road pavement, in which case the emitted particles are mechanically generated and mainly distributed in the coarse size fraction (Kreider et al., 2010), or by volatilization which results in the generation of much smaller particles, usually in the fine mode. The generation of fine particles is described as a thermo-mechanical process with local hot spots on the tyre tread reaching high temperatures and resulting in evaporation of the volatile content of tyres (Mathissen et al., 2011). Figure 11 displays near-spherical particles and agglomerates which probably originate from the carbon black reinforcing filler of the tyre (Dahl et al., 2006). The interaction of tyres and pavement alters both the chemical

composition and characteristics of the particles generated compared to the original tyre tread due to heat and friction, as well as incorporation of material from the road surface (Panko et al., 2013). Some researchers mention that pure tyre wear particles exist in very low quantities in the environment, while most of tyre wear particles are associated with road material (Fig. 12, ETRMA, 2014).

Fig. 11: Examples of particles generated by the road simulator and collected after a DMA set at 40 nm. The images were taken with TEM. Source: [Dahl et al., 2006]

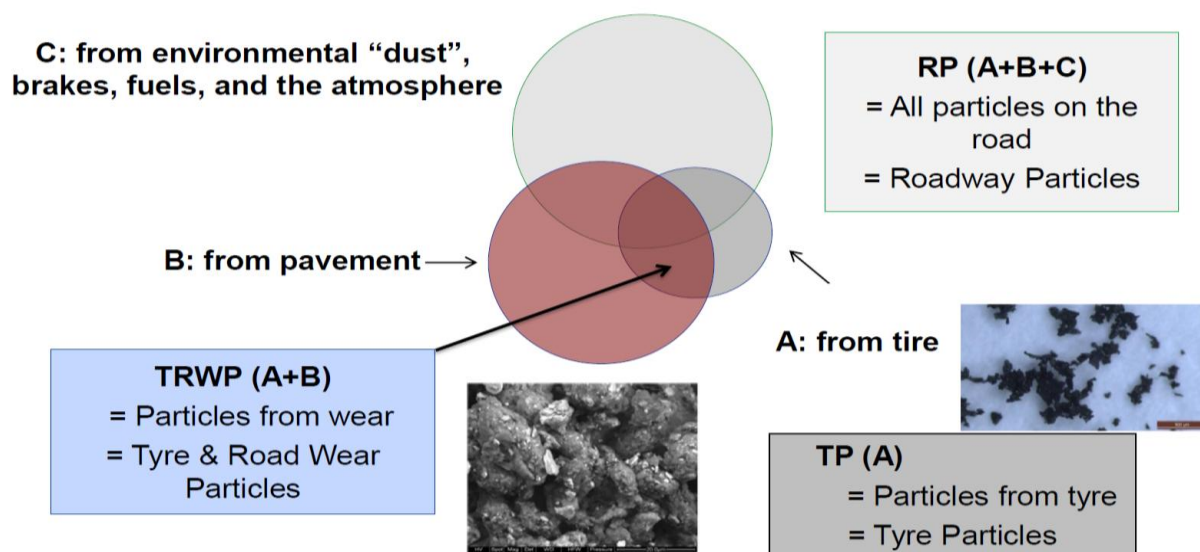


It is estimated that an average passenger vehicle tyre lasts for 40,000-50,000 km before it is worn out, with approximately 10-30% of its tread rubber emitted into the environment. The wear factor (defined as the total amount of material lost per kilometer) varies enormously depending on several parameters such as: a) **tyre characteristics** with the most important being size (radius/width/depth), tread depth, construction, pressure and temperature, contact patch area, chemical composition, accumulated mileage and set-up; b) **vehicle characteristics** such as weight, distribution of load, location of driving wheels, engine power, electronic braking systems, suspension type and state of maintenance; c) **road surface characteristics** with the most important being material (bitumen/concrete), texture pattern and wavelength, porosity, condition, wetness and surface dressing; d) **vehicle operation** such as speed, linear acceleration, radial acceleration, frequency and extend of braking and cornering (Boulter, 2006). For instance, heavy duty vehicles have been reported to emit approximately ten times higher tyre wear particles compared to light duty vehicles and passenger cars, while concrete pavements have been shown to produce lower wear emissions to PM₁₀ compared to other types of pavements (Amato et al., 2011; Denier van der Gon et al., 2012).

A wide range of chemicals can be found in vehicle tyres, depending on required performance standards and the manufacturing company. It has been reported that a common-sized all season passenger commercial tyre contains approximately 30 kinds of synthetic rubber, 8 kinds of natural rubber, 8 kinds of carbon black, steel cord for belts, polyester and nylon fibre, steel bead wire and 40 different chemicals, waxes, oils, pigments, silica and clays (Evans and Evans, 2006). Figure 13 provides a simplistic view of tyre layers and its generic composition into these layers. For commercial reasons it is unusual for tyre manufacturers to release exact details of tyre

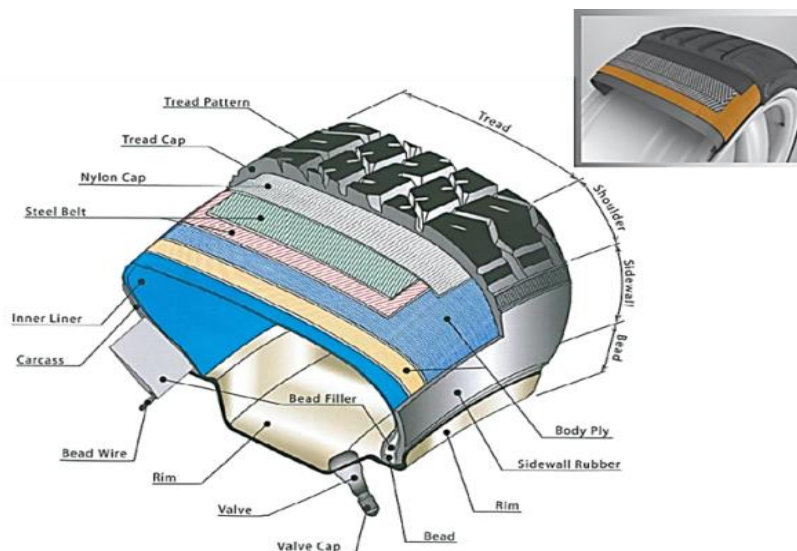
composition. In general, tread components consist of blends of different rubbers (41%) compounded with fillers (30%), reinforcing materials (15%), plasticizers (6%), chemicals for vulcanization (6%), and anti-aging agents (2%, Continental, 2012).

Fig. 12: Generalized scheme of particles generated from the interaction of tyre and pavement. Source: [ETRMA, 2014]



The bulk of tyre tread is composed of a variety of rubbers, including natural rubber co-polymers (NR), poly-butadiene rubber (PBR), styrene-butadiene rubber (SBR), nitrile rubber, neoprene rubber, isoprene rubber, and polysulphide rubber. The general composition of rubber blends commonly used in passenger vehicles is: natural rubber (40%), styrene-butadiene rubber (30%), butadiene rubber (20%), and other rubber (10%). Fillers are added to the rubber in order to improve its strength characteristics in terms of hardness and wear resistance. Carbon black has been commonly used as filler, but recently it has been partially substituted by other materials (silica incorporated with a silane coupling agent, carbon-silica dual-phase filler (CSDP) and "nanostructure" carbon blacks) in attempt to decrease rolling resistance without compromising strength and longevity. Vulcanizing agents (S, Se, Te, thiazoles, organic peroxides, nitro-compounds) typically make up 1% of the tyre rubber mass and are introduced in order to improve the durability of tyre rubber. Other chemicals used in the vulcanizing process are accelerators (Pb, Mg, Zn, sulphur compounds and calcium oxides) and retardants (terpene-resin acid blends). Anti-aging agents mainly comprise preservatives (halogenated cyanoalkanes), anti-oxidants (amines, phenols), anti-ozonants (diamines and waxes), and desiccants (calcium oxides). Plasticizers are used as softeners in order to provide elasticity and stickiness to the tyre. Commonly used plasticizers are synthetic organic oils and resins. For many years, one of the major components of extender oil was highly aromatic oil (HA), which contained a significant amount of PAHs in the range of 300–700 mg kg⁻¹ (Aatmeeyata et al., 2010). However, since 2010 the EU has required the discontinuation of the use of extender oils which contain more than 1 mg kg⁻¹ Benzo(a)pyrene, or more than 10 mg kg⁻¹ of the sum of all listed PAHs in the directive, in the manufacture procedure due to increased health concerns related to PAHs (European Commission, 2005).

Fig. 13: Simplistic view of tyre composition. Sources: [Evans and Evans, 2006; Continental, 2012]



In terms of absolute concentration ambient air contains about 0.2–11 $\mu\text{g m}^{-3}$ tyre particles, based on the highest concentrations of tyre markers reported in the literature (Cardina, 1974; Cadle and Williams, 1978; Kumata et al., 2000; Wik and Dave, 2009; Sjödin et al., 2010; Panko et al., 2013). Tyre wear contribution to PM_{10} has been reported to be significantly higher when studded tyres are employed and/or not well maintained porous pavements are used (Forsberg et al., 2005; Gustafsson et al., 2008; Denier Van der Gon et al., 2012). Studded tyres in Europe are used mainly in Nordic countries during the winter and have been found to generate a significant amount of wear particles at the interface between the tyre and the road surface. Studded tyres have been linked with violations of the European environmental quality standard for inhalable particles (PM_{10}), particularly in urban environments close to busy streets and roads (Forsberg et al., 2005; Gustafsson et al., 2008; Hussein et al., 2008).

Table 6: Literature estimations of the contribution of tyre wear particles to airborne PM (%)

Reference	PM_{10}	$\text{PM}_{2.5}$
Annema et al., 1996	5.0	-
Israël et al., 1994	10	-
Rauterberg-Wulff, 1999	8.6	-
Fausser, 1999	5.0	-
Hüeglin and Gehrig, 2000	1.0-7.5	-
Gualtieri et al., 2005	3.0-7.0	-
BLIC, 2005	6.0	3.0
Sjödin et al., 2010	0.1-3.9	-
Panko et al., 2013	0.84	-
Kwak et al., 2013	3-4	4-7

Not all generated tyre wear particles become airborne. A large proportion of the abraded rubber is released as relatively large particles ($>20\ \mu\text{m}$), and therefore is deposited on the road or very close to it. It is estimated that only 0.1-10% of the generated tyre wear particles become airborne (Boulter, 2006; Barlow et al., 2007; Gualtieri et al., 2008; Wik and Dave, 2009; Panko et al., 2013), although some researchers mention figures up to 30% (Luhana et al., 2004). In general, tyre wear is considered to be a significant source of non-exhaust traffic-related emissions (5-30% by mass), particularly at curbside sites, although this contribution may also include road wear as it is not easy to distinguish between these two sources (Lohmeyer et al., 2004; Boulter, 2006; U.S. EPA, 2009; Kreider et al., 2010; Amato et al., 2011; Harrison et al., 2012). On the other hand, tyre wear particle contribution to ambient PM_{10} have been reported to be low ($<1\%$ by mass, Panko et al., 2013), although some researchers have found higher contributions (up to 7% by mass), depending on the sampling site and the specific tracer used (Fauser, 1999; Rauterberg-Wulff, 1999; Gualtieri et al., 2005; Kwak et al., 2013).

Table 6 shows some literature estimates of tyre wear contribution to airborne PM_{10} (Panko et al., 2013). Based on these studies, it can be seen that tyre wear contribution to ambient PM_{10} varies greatly and may be a result of factors such as (ChemRisk, 2008):

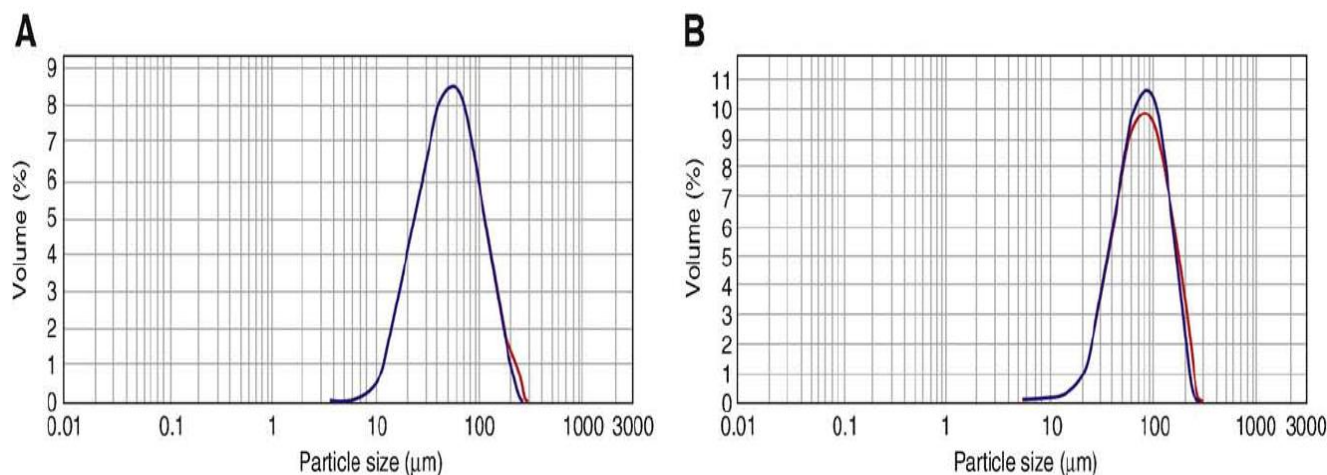
- ✓ Sampling methods as well as quantitative determination methods
- ✓ Use of different markers with a large range of error in reference materials
- ✓ The variable amount of polymer in tyre treads
- ✓ Different types of roads and vehicles as well as driving behavior
- ✓ Background concentrations and wind (direction and strength) between the sampling spots
- ✓ Type of sampling site (background, urban, etc.) and distance of sampling sites from the road
- ✓ Meteorological conditions and climate season

3.2 MASS DISTRIBUTION

Abrasion of tyre tread involves mechanical processes, which result in the emission of large ($>20\ \mu\text{m}$) and airborne particles in the coarse mode ($\text{PM}_{2.5-10}$), as well as thermo-mechanical and thermo-chemical processes (thermal degradation of tyre polymer, volatilization of extender oils and subsequent condensation of material in the ultrafine particle mode) when the tyre temperature exceeds 180°C (extreme cornering, unusual maneuvers, full stop braking), which result in the generation of very small particles in the fine and sometimes ultrafine mode (Fauser, 1999; Boulter, 2006; Mathissen et al., 2011). It is estimated that less than 10% (wt.) of tyre wear particles become airborne (Barlow et al., 2007; Gualtieri et al., 2008). Kreider et al. (2010) tested summer and friction tyres on asphalt based pavements on a road simulator and found that the size distribution by volume of collected tyre wear particles ranged between $5.0\ \mu\text{m}$ and $220\ \mu\text{m}$ and appeared a clear mode at $70\text{-}80\ \mu\text{m}$ (Fig. 14B). The corresponding size distribution of on-road generated wear particles collected under normal driving conditions (steady state driving, acceleration/deceleration $< 2\ \text{m s}^{-2}$) was similar with the mode centered at $50\ \mu\text{m}$ (Fig. 14A). It should be noticed that in both studies the particle size distribution was truncated below $0.3\ \mu\text{m}$ due to instrument limitations. Similar observations were made by Smolders and Degryse (2002), who found roadside tyre debris

with a mean diameter of 65 μm for passenger vehicles and 80 μm for trucks. These findings suggest that most of the material emitted during the tyre wear process will not remain airborne for very long. On the other hand, airborne tyre wear particles can be divided according to their size into fine and coarse particles. This distinction of airborne tyre wear particles was firstly recorded in studies conducted in the 1970s (Cardina, 1974; Cadle and Williams, 1978), while the presence of finest fraction was also confirmed by several researchers in more recent work (Dahl et al., 2006; Mathissen et al., 2011). The relative mass contributions of these two dominant modes appear to be variable and dependent on various conditions (Boulter, 2006). Aatmeeyata et al. (2009) reported that approximately 32% of tyre wear PM_{10} mass is found in sizes below 1.0 μm , when non-studded tyres are tested against concrete roads, while Kupiainen et al. (2005) found a 15% contribution of fine particles in total PM_{10} mass when friction and studded tyres are tested against asphalt concrete. Older data mention significantly higher contributions of small particles with almost 70% by mass of tyre wear PM_{10} being classified as $\text{PM}_{2.5}$, 10% as $\text{PM}_{1.0}$, and 8% as $\text{PM}_{0.1}$ (Berdowski et al., 1997). Similarly, Fauser (1999) found a significant part of tyre wear PM_{20} in atmospheric samples (92% by mass) to lie in sizes smaller than 1.0 μm . In any case, tyre wear is often examined in conjunction with the pavement material, therefore actual PM_{10} tyre wear emissions are affected by several factors such as pavement construction, rock material properties, as well as pavement's state of maintenance (Denier Van der Gon et al., 2012). It should be pointed out that tyre rubber has the tendency to develop electrostatic charge leading to a fraction of the particles being adhered to vehicle surfaces, and thus affecting the study of particle size distributions (Thorpe and Harrison, 2008).

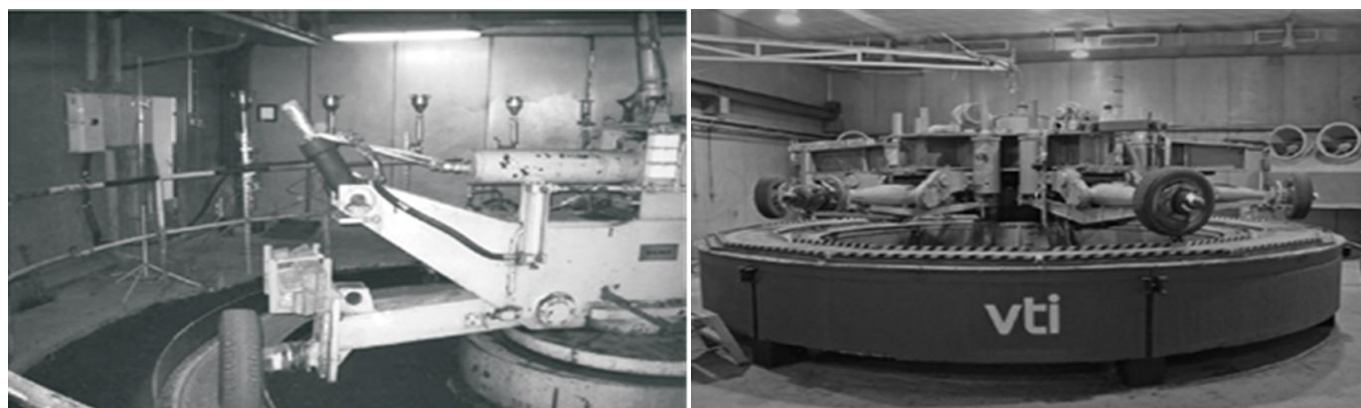
Fig. 14: Particle size distribution determined by volume of particles according to laser diffraction for road particles (A) and tyre wear particles (B). Source: [Kreider et al., 2010]



In general, three kind of studies regarding tyre wear particles characterization can be found in the literature: those which investigate particles by direct measurement using a simulated wheel in the laboratory (Fig. 15, Kupiainen et al., 2005; Dahl et al., 2006; Gustafsson et al., 2008; Panko et al., 2009; Kreider et al., 2010), those which perform sampling and analysis of PM in ambient air followed by application either of source apportionment methods (Luhana et al., 2004; Bukowiecki et al., 2009a) or specific tyre wear tracers (Harrison et al., 2012; Panko et al., 2013), and those which sample tyre wear particles on-road under “real world” driving conditions by means of mobile units (Hussein et al., 2008; Mathissen et al., 2011). Road simulation laboratory studies are employed in order to study the contributions from tyre and road wear in an isolated environment, under controlled laboratory conditions, whereas the mobile units usually measure additionally the

contribution from resuspended dust present under ambient conditions (Kumar et al., 2013). All studies indicate that the emissions depend on various parameters such as the characteristics of the road surface, the tyre and the vehicle tested. In receptor modeling, variations in the above parameters are difficult to consider and modeling results may be applicable to a specific site only (Aatmeeyata et al., 2009). Table 7 provides a brief overview of the most important literature studies dealing with the characterization of tyre wear particles in terms of their mass size distribution.

Fig. 15: Test room with the rotating axle system in the foreground and the impactor inlets in the back (left) and the VTI road simulator (right). Sources: [Left - Kupiainen et al., 2005; Right - Gustafsson et al., 2008]



Gustafsson et al. (2008) performed road simulation studies on friction and studded tyres against different asphalt materials and determined the mass size distribution of tyre wear PM_{10} by means of APS. Friction tyres exhibited a bimodal PM_{10} mass size distribution with peaks at approximately 2-3 μm and 8-9 μm (Fig. 16), while studded tyres appeared a rather unimodal distribution with a peak at 5-6 μm . PM_{10} mass was distributed in the coarser fraction of PM_{10} with studded tyres, while on the other hand, PM_{10} concentrations were significantly lower with friction tyres. They also found that the shape of mass size distributions was not strongly affected by speed, in contrary to the total particle concentration which increased with increasing speed. Similarly, Aatmeeyata et al. (2009) developed a fully enclosed laboratory-scale model and tested friction tyres (used in two and three-wheelers, as well as in small cars) against concrete asphalt pavement. PSA measurement revealed a bimodal tyre wear PM_{10} distribution with the two modes at 300-400 nm and 4-5 μm , respectively (assuming a particle density of 2.53 g cm^{-3}). They also reported that the peak found at 0.3 μm could possibly be artificial since the particle size distribution is truncated below 0.3 μm (the GRIMM sampler had a particle size limit at 0.3 μm). A clear bimodal PM_{10} mass size distribution with peaks at 1.0 μm and 5-8 μm was also reported by Panko et al. (2009) in a road simulation study conducted with summer and winter tyres against a dense asphalt pavement (APS - Fig. 16).

On the other hand, Kupiainen et al. (2005) tested friction and studded tyres on an asphalt concrete pavement and found different mass size distributions, depending on the type of tyre and the speed. Lower speeds (15 km h^{-1}) were associated to bimodal mass size distribution at least for studded tyres with the modes at approximately 1.0 and 10 μm , while higher speeds (30 km h^{-1}) were accompanied by a rather unimodal distribution with a distinct peak at 9-10 μm (Fig. 17). Unimodal distributions were also reported by Sjödin et al. (2010) for all types of tyres tested on stone mastic asphalt. They found that the coarse fraction as measured by the APS makes up most of the mass of PM_{10} . In brief, for the studded tyres the size mode peaked at 3-4 μm , while for winter tyres the peak

of the PM concentration was shifted at 2–4 μm . Summer tyres resulted in low concentrations of fine particles and peaked at approximately 2 μm .

Fig. 16: Bimodal mass distributions of particles generated from friction tyres running against different asphalt pavements. Sources: [Left - Gustafsson et al., 2008; Right - Panko et al., 2009]

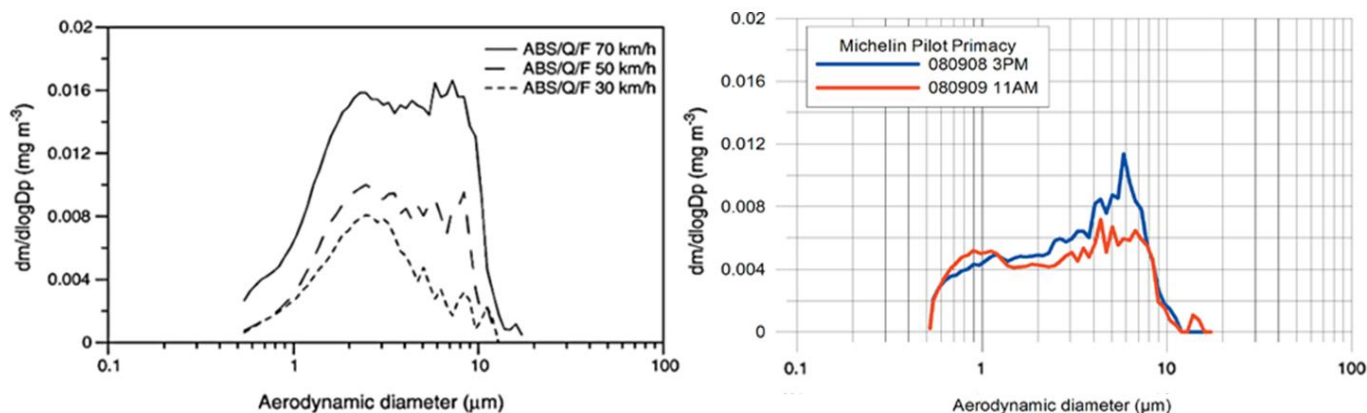
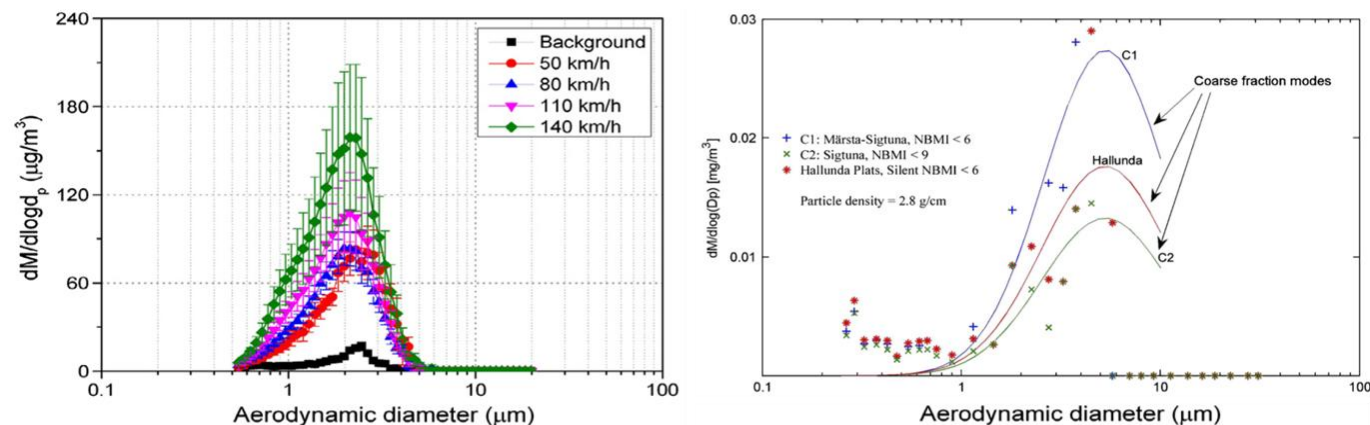


Fig. 17: Unimodal mass distributions of particles generated from friction tyres running against different asphalt pavements. Sources: [Left - Kwak et al., 2013; Right - Hussein et al., 2008]



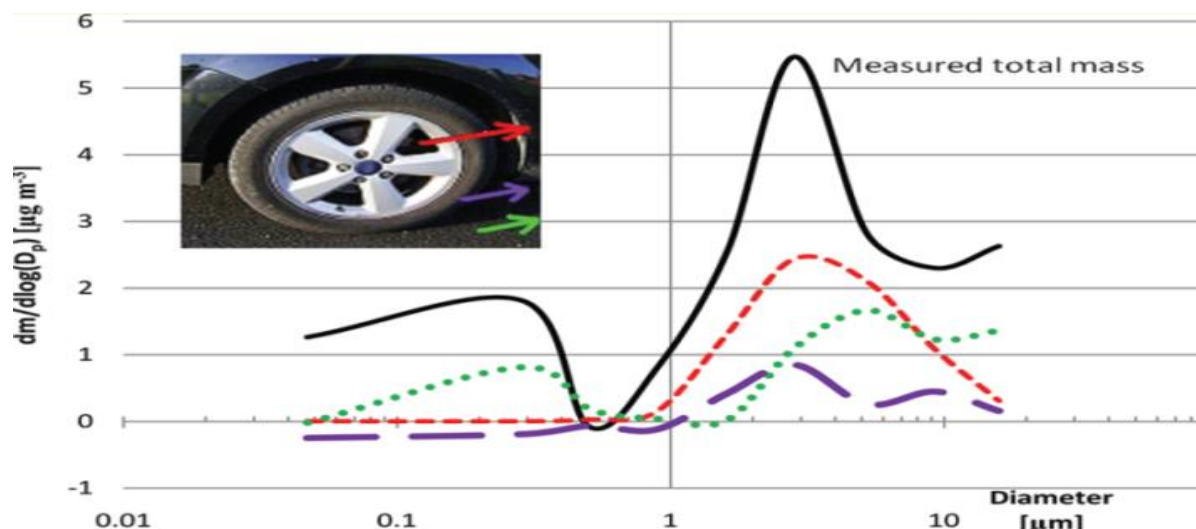
Regarding measurement of ambient PM, Harrison et al. (2012) collected size-fractionated samples of airborne PM (<0.2 μm to >21 μm) and used the size distribution of specific tracer elements in order to estimate the contributions of non-exhaust sources to particle mass. Fig. 18 shows that tyre wear particles exhibited a bimodal PM₁₀ mass distribution with peaks at 2.5 μm and 9-10 μm , respectively (purple line). Hussein et al. (2008) used a small van to perform on-road measurements in order to investigate the factors affecting non-tailpipe emissions from paved roads and found a coarse particle mode with a mean diameter of 3-5 μm for all types of tyres and pavements (stone mastic asphalt, dense asphalt concrete) tested (Fig. 17). They concluded that this mode is similar to the one reported for tyre wear samples in previously conducted road simulation studies (Gustafsson et al. 2008). However, it should be pointed out that Hussein et al. (2008) did not use any tool to specify the source of these particles, thus they could be a result of tyre or/and road surface abrasion, as well as of road dust resuspension.

Table 7: Review of literature studies regarding the mass distribution of airborne tyre wear particles

Reference	Type of study	Tested	Method	Mass Size Distribution
Kupiainen et al. 2005	Road simulation study	Friction-studded tyres on asphalt concrete	Cascade impactor	Unimodal and Bimodal (1.0 μm & 10 μm)
Gustafsson et al. 2008	Road simulation study (VTI facilities)	Friction-studded tyres on stone mastic and dense concrete asphalts	APS (> 0.5 μm)	Bimodal (2.5 μm & 8-9 μm)
Aatmeeyata et al. 2009	Road simulation study	Summer tyres on concrete road	GRIMM Analyzer (> 0.3 μm)	Bimodal (0.3 μm & 4-5 μm)
Panko et al. 2009	Road simulation study (VTI facilities)	Summer-friction tyres on dense asphalt pavement	APS (> 0.5 μm)	Bimodal (1.0 μm & 5-8 μm)
Sjödín et al. 2010	Road simulation study (VTI facilities)	Summer-friction-studded tyres on stone mastic asphalt	APS (> 0.5 μm)	Unimodal (2-4 μm)
Kreider et al. 2010	Road simulation study	Summer-friction tyres on standardized asphalt concrete	Laser diffraction (> 0.3 μm)	Unimodal (75 μm)
Hussein et al., 2008	On-road direct measurement	All types of tyres on stone mastic and dense concrete asphalts	GRIMM Analyzer (> 0.265 μm)	Unimodal (3-5 μm)
Kreider et al. 2010	On-road direct measurement	Summer-friction tyres on asphalt based pavements	Laser diffraction (> 0.3 μm)	Unimodal (50 μm)
Harrison et al., 2012	On-road measurement by modelling	Roadside PM attributable to non-exhaust emissions	Sampling not included volatile material (MOUDI)	Bimodal (2.5 μm & 10 μm)
Kwak et al., 2013	On-road direct measurement	Friction tyres on asphalt concrete	Cascade impactor (> 0.5 μm)	Unimodal (2-3 μm)

Literature results are at variance regarding the mass size distribution of tyre wear particles and more particularly regarding the presence of a second mode in the fine size fraction. Differences in the parameters (type of tyre, vehicle load and speed, type of pavement, experimental assembly, etc.) make comparisons more difficult. However, most studies report bimodal mass size distribution with one peak lying among the fine mode and the other among coarse mode, while some others mention only one peak which could be a result of limitations in sampling and analysis instrumentation.

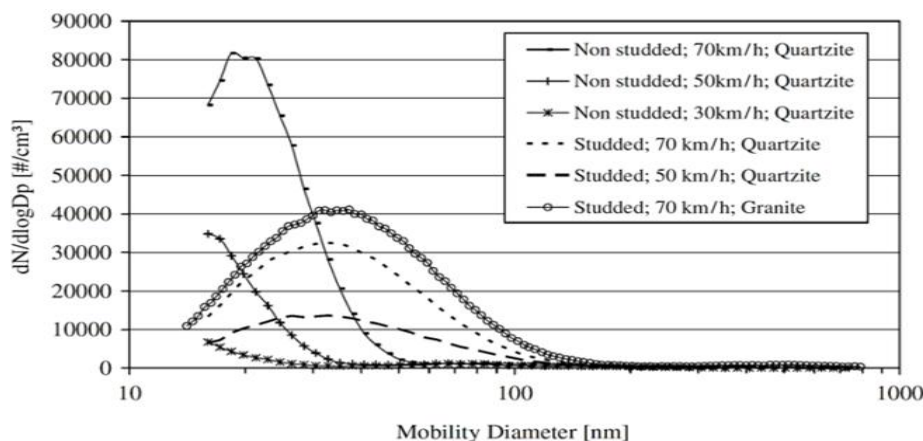
Fig. 18: Reconstruction of micrometer particle mass through scaling of tracer elements.
Source: [Harrison et al., 2012]



3.3 PARTICLE NUMBER DISTRIBUTION

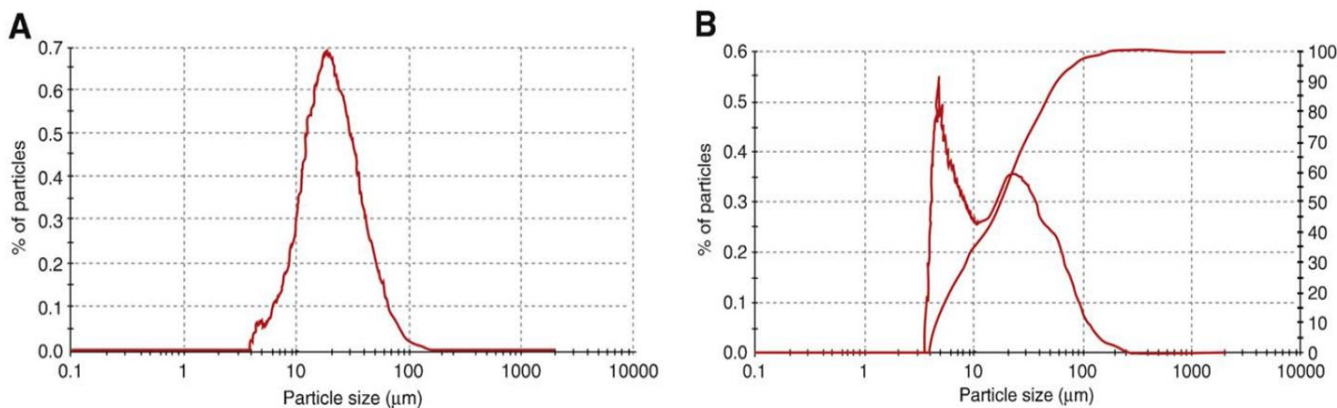
In order to understand and characterize particles generated from tyre wear it is necessary to study their PN distributions. Although there are some studies which do not report UF particle generation under “normal driving conditions” (Hussein et al., 2008; Kreider et al., 2010; Mathissen et al., 2011; Panko et al., 2013), there are other studies which have reported a significant presence of ultrafine particles in tyre wear PM_{10} , regardless the tyre and pavement tested (Kupiainen et al., 2005; Dahl et al., 2006; Gustafsson et al., 2008; Aatmeeyata et al., 2009; Panko et al., 2009). Most of these studies were performed in the laboratory under well controlled conditions which exclude the possibility of contamination from other sources. For instance, Dahl et al. (2006) performed a road simulation study with studded and friction tyres against different kinds of asphalts and, despite the limitation of 15 nm in particle size detection (SMPS), they found a significant ultrafine mode with a peak between 15–50 nm, depending on the type of tyre and pavement tested (Fig. 19). They also found that the particle size distribution shifts towards smaller diameters when friction tyres are tested (with maxima being at <20 nm for friction tyres and at 40 nm for studded tyres). Finally they noticed that more particles are generated when higher speeds are applied. They concluded that wear particles more likely originate from the tyres, since the particle size distribution and source strength is dependent on the type of tyre (Gustafsson et al., 2008). A similar mode was reported by Panko et al. (2009) in their road simulation study performed with friction tyres against a dense asphalt pavement representative of typical central European roads, with however the measured peak being consistent with the background concentrations routinely measured. Aatmeeyata et al. (2009) tested friction tyres against concrete asphalt pavement in order to investigate wear particle’s number distribution in the size range of 0.3–10 μm , and found a bimodal distribution with maxima at 0.33 and 1.7 μm (particle size limit at 0.3 μm with the GRIMM Particle Size Analyzer). They concluded that the peak at 0.3 μm could possibly be artificial and include many smaller particles. It should be noticed that actual distributions may be affected or even altered by the tendency of tyre rubber to develop electrostatic charge, which leads to a fraction of the particles adhering to vehicle surfaces and not being sampled (Thorpe and Harrison, 2008). Table 8 provides a brief overview of the most important literature studies dealing with the characterization of tyre wear particles in terms of their particle number distribution.

Fig. 19: PN size distributions of the aerosol generated at with different tyres on different pavements. Sources: [Dahl et al., 2006; Gustafsson et al., 2008]



On the other hand, Kreider et al. (2010) tested summer and friction tyres on asphalt based pavements both on-road and in the laboratory and found no ultrafine particles under controlled driving conditions. Their study included bigger wear particles and they reported a unimodal PN distribution for road collected particles with a clear mode at approximately $25 \mu m$ (Fig. 20A) and a bimodal PN distribution for laboratory generated particles with the first mode at $5 \mu m$ and the second at $25 \mu m$ (Fig. 20B). Sjödín et al. (2010) tested all types of tyres on stone mastic asphalt and reported no ultrafine particle generation for winter and summer tyres. Only in case of studded tyres they found a peak in the PN distribution at 30 nm.

Fig. 20: PN size distributions for road particles (A) and laboratory generated particles (B) as determined by transmission optical microscopy. Source: [Kreider et al., 2010]



Mathissen et al. (2011) investigated the potential generation of very small and UF particles (5.6-562.3 nm) from the tyre road interface during real world driving by testing summer tyres on a regular asphalt road. For normal driving conditions (i.e. steady-state at 50, 70, 100 and 120 $km\ h^{-1}$, cornering on a cycle with $d= 48\ m$ at 30 $km\ h^{-1}$ and lateral acceleration of $2.9\ m\ s^{-2}$, accelerations up to $2.4\ m\ s^{-2}$, braking with $< 3\ m\ s^{-2}$) no enhanced particle number concentration in the UF size range was observed. On the other hand, extreme driving conditions (i.e. cornering on a cycle with $d= 48\ m$ at 46-48 $km\ h^{-1}$ and lateral acceleration of $8.0\ m\ s^{-2}$, accelerations with racing start) resulted in elevated ultrafine PN concentrations compared to the background measurement. The authors

reported that it was unclear whether the particles originated from the tyres or the road surface or both since no chemical particle analysis was conducted (Fig. 21).

Fig. 21: PN size distributions from the EEPS for different maneuvers. Source: [Mathissen et al., 2011]

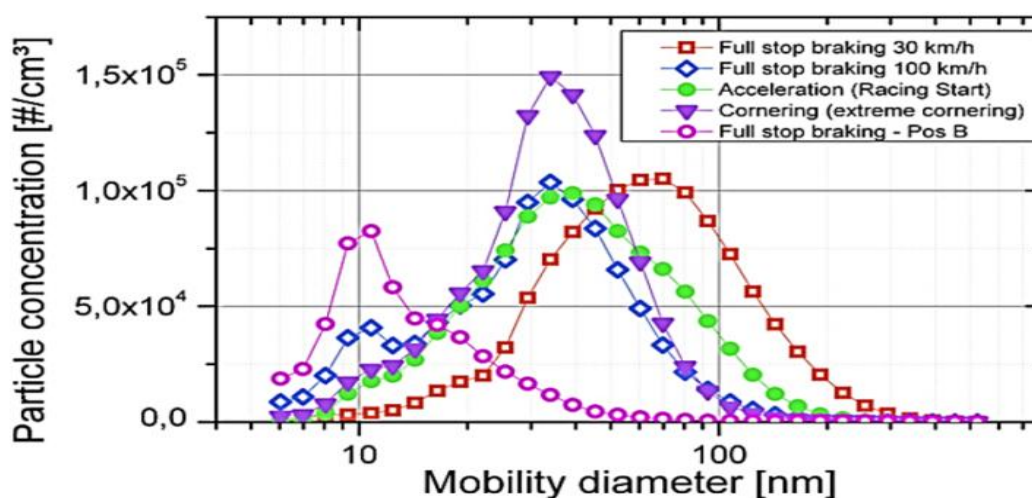


Table 8: Review of literature studies regarding the particle number distribution of airborne tyre wear particles

Reference	Type of study	Tested	Method	Particle Number Distribution
Dahl et al. 2006	Road simulation study	Friction-studded tyres on stone mastic and dense concrete asphalts	SMPS	Unimodal (15-50 nm)
Gustafsson et al. 2008	Road simulation study	Friction-studded tyres on stone mastic and dense concrete asphalts	SMPS	Unimodal (15-50 nm)
Aatmeeyata et al. 2009	Road simulation study	Summer tyres on concrete road	GRIMM Analyzer (> 0.3 µm)	Bimodal (0.3 µm & 1.7 µm)
Panko et al. 2009	Road simulation study	Summer-friction tyres on dense asphalt pavement	SMPS	Unimodal (30-90 nm)
Kreider et al. 2010	Road simulation study	Summer-friction tyres on standardized asphalt concrete	Laser Diffraction & TOM (> 0.3 µm)	Bimodal (5 µm & 25 µm)
Sjödin et al. 2010	Road simulation study	Summer-friction-studded tyres on stone mastic asphalt	SMPS	Unimodal (30 nm) only for studded
Kreider et al. 2010	On-road direct measurement	Summer-friction tyres on asphalt based pavements	Laser Diffraction & TOM (> 0.3 µm)	Unimodal (25 µm)
Mathissen et al. 2011	On-road direct measurement	Summer tyres on regular asphalt road	(< 0.56 µm)	Fig. 21

Overall, a noticeable peak in the ultrafine mode has been reported by some researchers accompanied with a tendency of the PN distribution to shift towards lower values when friction tyres are used. However, these findings are still under strong debate.

3.4 CHEMICAL CHARACTERIZATION

A wide range of chemical compounds are employed in the manufacture of commercial tyres depending on the type of vehicle and their required performance standards. In brief, a large variety of rubber hydrocarbons comprise the bulk of tyre tread, while carbon black and Si are also employed in high abundances mainly as fillers but also for other purposes. Additionally, S, Se, Te, thiazoles, organic peroxides, nitro- and azo- compounds are often used as vulcanizing agents, while sulphur compounds, along with Ca, Pb, Mg and mainly Zn oxides, are employed as accelerators during the vulcanization procedure. Other chemicals include a wide variety of organic compounds such as terpene-resin acid blends, synthetic organic oils and tars, halogenated cyanoalkanes, amines, diamines, phenols, as well as inorganic substances like calcium oxide (Boulter, 2006). A very detailed chemical composition of tyres regarding trace elements and PAHs is provided by Han Ten Broeke et al., (2008).

As far as inorganic compounds are concerned several trace elements (Si, Al, Ca, Ti, S, K, Cu, Fe, Pb, Mg, Te, Se, Cd) which are used in tyre manufacture have been identified in airborne wear particles generated in the tyre-pavement interface (Boulter, 2006; Thorpe and Harrison, 2008). Gustafsson et al. (2008) tested friction and studded tyres against different kind of pavements and found that Al and Si dominated airborne wear particles. Kupiainen et al. (2005) tested studded and friction tyres against granite pavements and found a significant number (90%) of airborne wear particles comprising of Al and Si. Similar results were reported by Panko et al. (2009) who found that Si dominated wear particles in a road simulation study conducted with friction tyres. In all studies the majority of these particles were attributed to pavement wear. For Si, it has been proposed that only a relatively small mass contribution comes from the tyres. Regarding tyre generated elements, S displayed a significant enrichment in the sub-micrometer stages, particularly when friction tyres were tested (Gustafsson et al., 2008; Panko et al., 2009). Also, tyre wear particles are considered to be a significant source of Zn, particularly in urban areas (Hjortenkrans et al., 2007; Wik and Dave, 2009; Harrison et al., 2012). Tyres contain about 1% Zn, which is present either as inorganic Zn (ZnO and ZnS) or in the form of organic compounds (Fauser, 1999; Dahl et al., 2006; Pant and Harrison, 2013). Gustafsson et al. (2008) found Zn to be extremely enriched for all particle sizes (PM₁₀), particularly when friction tyres are tested. Panko et al. (2009) reported significant Zn contributions to the total particle mass especially for particles smaller than 2 µm (PIXE, Fig. 22). Apegyei et al. (2011) concluded that Zn concentrations deriving from tyres are about one order of magnitude higher than those of brakes. Zn is also present in high concentrations in larger particles. For instance, Kreider et al. (2010) found similar Zn contributions to the total particle mass (0.3-0.4%) both for road collected and laboratory generated wear particles (0.3-150 µm), while Smolders and Degryse (2002) found slightly higher Zn contributions to the tyre wear mass (<100 µm) of passenger vehicles (1.1%) and trucks (2.4%). Gadd and Kennedy (2000) also reported Zn in passenger vehicles tyre tread ranging between 0.6-1.0%. As seen in Table 9, several researchers have used Zn as a tyre wear particle tracer (Adachi and Tainosho, 2004; Amato et al., 2011; Apegyei et al., 2011; Harrison et al., 2012), however this is under questioning due to the fact that there have been recognized several different sources of Zn in the environment (industrial activities,

brake wear, automobile exhaust, lubricants, galvanized road furniture, metallic barriers). In some cases extractable organic Zn has been used as a tyre wear tracer since the only probable interfering source seems to be engine lubricants (Fauser, 1999; Wik and Dave, 2009).

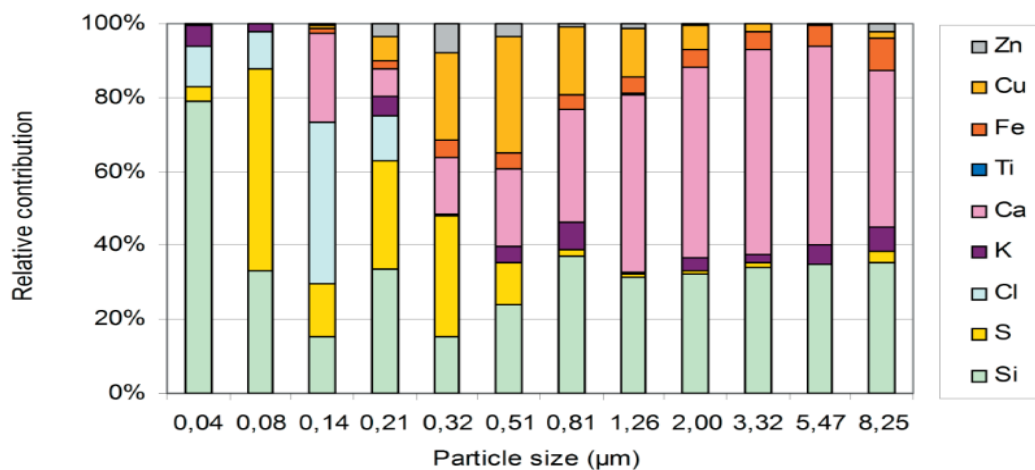
Table 9: Most common organic and inorganic key tracers employed for identification of tyre wear particles

Reference	Inorganic Tracer	Reference	Organic Tracer
Adachi et al., 2004	Zn	Cadle and Williams, 1978	SBR
Tanner et al., 2008	Zn	Fauser, 1999	Organic Zn, SBR
Keuken et al., 2010	Zn	Kumata et al., 2000	BTs
Amato et al., 2011	S, Zn	Kumata et al., 2002	BTs
Apegyei et al., 2011	Zn, Ca, W, K, Fe, Ti, Cr, Mo	Ni et al., 2008	BTs
Duong and Lee, 2011	Zn	Kreider et al., 2010	SBR, BR, NR
Song and Gao, 2011	Zn, Co	Amato et al., 2011	OC
Harrison et al., 2012	Zn	Panko et al., 2013	SBR, BR, NR

Tyre rubber is predominantly composed of organic compounds, with styrene and butadiene polymers being the dominant species. Regarding tyre wear PM₁₀, Kupiainen et al. (2005) found that they comprise approximately of 5% carbonaceous compounds. The carbonaceous fraction was dominated by organic substances (88%), with trace amounts of elemental (4%) and carbonate carbon (8%). They also concluded that friction and studded tyres generate particles with similar organic carbon content. Based on their morphology Dahl et al. (2006) examined UF particles generated from the interaction of tyres and pavements and found that they have very heterogenic forms such as carbon chains, droplets and granules. They concluded that these particles seem to have rather an organic origin (softening filler and specifically mineral oils), indicating different sources compared to coarser particles (Gustafsson et al., 2008). Similarly, Panko et al. (2009) found that most of the particles within the fine fraction mode have a composition which includes strong carbon peak, while these particles display a variety of shapes when observed at the SEM. Despite that PAHs are frequently examined in ambient PM₁₀ due to increased health concerns, no studies regarding PAHs concentrations in tyre wear PM₁₀ were found. In larger particles (>10 µm) high concentrations of pyrene, phenanthrene and fluoranthene have been reported by Aatmeeyata and Sharma (2010) in agreement with previous published results (Rogge et al., 1993; Gadd and Kennedy, 2000), while Kreider et al. (2010) concluded that total PAHs content in tread wear particles was only 5% of the total PAH content of the road wear particles, with other sources such as natural, asphalt, automobile exhaust and fuel combustion products being the dominant PAH contributor (Kumar et al., 2013). Aatmeeyata and Sharma (2010) also concluded that PAH emissions increase with increasing mileage of the tyre, with Kwon and Castaldi (2012) enhancing these observations by examining the mechanism of PAHs generation from the thermal degradation of tyres. Benzothiazoles (BTs, benzothiazole and its derivatives) is another chemical group commonly found in tyre wear particles. Besides tyres, benzothiazoles are also present in antifreeze products with, however, significantly lower contributions to ambient concentrations (0.0004–4%). For that reason BTs have been widely used as specific tracers for tyre wear (Boulter, 2006; Thorpe and Harrison, 2008; Wik and Dave, 2009). Various other organic compounds have been identified in

tyre tread samples with the most common being n-alkanes, n-alkanoic acids and natural resins (Rogge et al., 1993). It was also proposed that n-alkanes with more than 35 carbons would be a useful marker for tyre wear, since these compounds have very few urban emission sources other than tyre wear (Boulter, 2006). Styrene butadiene rubber (SBR) has also been used as a tyre tread marker since more than 70% of its global production is used in tyre manufacturing, thus minimizing the contribution from other sources (Wik and Dave, 2009; Panko et al., 2013).

Fig. 22: Analysis of airborne tyre wear particles by means of PIXE. Source: [Panko et al., 2009]



3.5 EMISSION FACTORS

Tyres can lose up to 10% of their mass during their lifetime (Milani et al., 2004), while less than 10% of tyre wear material is expected to be emitted as PM₁₀ under “normal” driving conditions (Boulter, 2006). Speed, type of tyre, road surface type and driving conditions have been reported as influential parameter for tyre wear emissions (Gustafsson et al., 2008; Mathissen et al., 2011; Pant and Harrison, 2013). In order to determine tyre wear PM EFs both direct measurements from the sources (i.e. on-road samplings, road simulation studies), as well as modeling have been employed.

Kupiainen et al. (2005) reported a PM₁₀ EF of 9.0 mg km⁻¹ vehicle⁻¹ for friction tyres, Sjödin et al. (2010) a PM₁₀ EF of 3.8 mg km⁻¹ vehicle⁻¹ for summer tyres and Panko et al. (2013) a PM₁₀ emission rate of 7.0 mg km⁻¹ on an on-road study. These values are close to older PM₁₀ emission factors reported by U.S. EPA for light-duty vehicles (5.0 mg km⁻¹ vehicle⁻¹), and within the range of 6.0 and 9.0 mg km⁻¹ vehicle⁻¹ reported by Rogge et al. (1993). On the other hand, studded tyres EFs have been reported to be significantly higher with Sjödin et al. (2010) reporting a PM₁₀ EF of 350 mg km⁻¹ vehicle⁻¹. It is concluded that friction tyre PM₁₀ EFs for light duty vehicles deriving from direct measurements fall in the range of 3.8-9.0 mg km⁻¹ vehicle⁻¹.

Rauterberg-Wulff (1999) determined tyre wear PM₁₀ emission factors by means of receptor modeling in a study conducted in the Berlin-Tegel tunnel, and found EFs for LDVs and HDVs of 6.1 mg km⁻¹ vehicle⁻¹ and 31 mg km⁻¹ vehicle⁻¹, respectively. Similarly, the Regional Air Pollution Information and Simulation (RAINS) model calculated PM₁₀ EFs for tyre wear of 6.5 mg km⁻¹ vehicle⁻¹ (LDVs) and 40 mg km⁻¹ vehicle⁻¹ (HDVs). Additionally, PM_{2.5} EFs of 0.3 mg km⁻¹ vehicle⁻¹ (LDVs) and 2.0 mg km⁻¹ vehicle⁻¹ (HDVs) were reported in the same project (Panko et al., 2013). Hüglin and Gehrig, (2000) determined a much higher tyre wear EF (13.0 mg km⁻¹ vehicle⁻¹) for

passenger vehicles in Switzerland, while PCA was employed during the PARTICULATES project and an average tyre wear factor of $74 \text{ mg km}^{-1} \text{ vehicle}^{-1}$ was derived for passenger vehicles (Luhana et al., 2004). It has to be pointed out that this EF refers to total tyre wear particles and not PM_{10} , but with the assumption of 10% of tyre wear becoming airborne it corresponds to a PM_{10} EF of $7.4 \text{ mg km}^{-1} \text{ vehicle}^{-1}$ (Boulter, 2006). NAEI provided generalized non-exhaust emission factors for each main vehicle type in the UK fleet averaged overall all road types. Regarding passenger vehicles they reported a PM_{10} tyre wear EF of $7.0 \text{ mg km}^{-1} \text{ vehicle}^{-1}$, while for $\text{PM}_{2.5}$ the corresponding EF was $5.0 \text{ mg km}^{-1} \text{ vehicle}^{-1}$. In case of rigid HGVs they found EFs of 17.0 (PM_{10}) and $12.0 \text{ mg km}^{-1} \text{ vehicle}^{-1}$ ($\text{PM}_{2.5}$), and for artic HGVs 35.0 and $25.0 \text{ mg km}^{-1} \text{ vehicle}^{-1}$, respectively (NAEI, 2012). On the other hand, Abu-Allaban et al. (2003) employed chemical mass balance receptor modeling in order to determine wear EFs at roadside locations, but they observed no contribution from tyre wear. They concluded that this may have been a result of the electrostatic charge carried by tyre wear particles which prevented them from accumulating on filters during sampling. Similarly, there have been several other studies which failed to identify tyre wear in PM_{10} , probably due to the lack of a unique chemical tracer for tyre wear and difficulties in distinguishing tyre from road wear (Bukowiecki et al., 2009a; Lawrence et al., 2013). Overall, a PM_{10} tyre wear EF of approximately $6.0\text{-}7.5 \text{ mg km}^{-1} \text{ vehicle}^{-1}$ is estimated for passenger vehicles in good agreement with direct measurements (Table 10).

Table 10: PM_{10} emission factors of tyre wear reported in the literature for LDVs and passenger cars ($\text{mg km}^{-1} \text{ vehicle}^{-1}$)

Reference	Type of study	PM_{10} EF
USEPA, 1995	Emissions Inventory	5.0
Keuken et al., 1999	Emissions Inventory	5.0
Rauterberg-Wulff, 1999	Receptor modelling	6.1
Hüeglin and Gehrig, 2000	Receptor modelling	13
Lukewille et al., 2001	Receptor modelling	6.5
CEPMEIP, 2002	Emissions Inventory	4.5
Luhana et al., 2004	Receptor modelling	7.4
Kupiainen et al., 2005	Road simulation study	9.0
Ten Broeke et al., 2008	Emissions Inventory	8.0
Sjödin et al., 2010	Road simulation study	3.8
CEPMEIP, 2012	Emissions Inventory	4.5
NAEI, 2012	Emissions Inventory	7.0
Panko et al., 2013	On-road study	2.4
AVERAGE VALUE		6.3

3.6 HEALTH RELEVANCE

There are several in-vitro and animal studies which have investigated the possible link between airborne tyre wear particles and negative health impacts, with some of them showing contradictory

results. Besides the generalized discussion regarding the way that size and chemical composition of PM may pose adverse impacts on human health, there are still many questions regarding the possible mechanisms which may render tyre wear particles potentially toxic.

Gustafsson et al. (2008) conducted cell studies on wear particles sampled from road simulation tests and found that particles generated from the interaction of studded tyres and asphalt pavements are almost as inflammatory as particles from an urban street, and at least as inflammatory as particles from diesel exhaust. They observed that these particles are able to induce inflammation in airways depending on the type of stone material used in pavement. Lindbom et al. (2006) also demonstrated that studded tyre wear particles are able to induce pro-inflammatory events in macrophages, such as secretion of interleukin-6, interleukin-8, and tumor necrosis factor- α from human monocyte-derived macrophages. Karlsson et al. (2011) conducted road simulation tests and examined the toxicoproteomic effects on human monocyte derived macrophages after exposure to wear particles generated from the interface of studded tyres and a granite-containing pavement. They found that proteins associated with inflammatory response were increased, and proteins involved in cellular functions such as redox balance, anti-inflammatory response, and glycolysis were decreased. Briefly, studded tyre wear particles have been shown to have considerable pro-inflammatory potential and profound effects on macrophages *in vitro*, although many details of their action remain to be clarified (Karlsson et al., 2011).

The toxicity of tyre particle leachates in laboratory animals and *in vitro* tests has been mainly attributed to Zn, as well as to the extractable organic compounds present in tyre wear particles (Gualtieri et al., 2005; Mantecca et al., 2007; Wik and Dave, 2009). Tyre particle leachates which have undergone chelation (a method of removing certain heavy metals from various matrices), or passed through a cation exchange resin, exhibited reduced toxicity potential to *Daphnia magna*, *Pseudokirchneriella subcapitata* and *Ceriodaphnia dubia* compared to untreated leachates. This suggests the presence of toxic metals (i.e. Zn) in the tyre particle leachates, as well as their toxicity to the tested organisms (Gualtieri et al., 2005; Wik and Dave, 2009). Additionally, higher concentrations of Zn in tyre particle leachates resulted in increased toxic responses, thus indicating that Zn is among the metals posing the observed toxic effects (Wik and Dave, 2009). In general, Zn has been associated with adverse health effects in humans and particularly acute respiratory responses. For instance, Claiborn et al. (2002) examined the effects of particulate metals on emergency room admissions for asthma and respiratory problems, and observed a significant association between emergency room admissions for asthma and particulate Zn. Apeagyei et al. (2011) suggested that the relatively high level of Zn and Cu concentrations in a study conducted in Massachusetts can lead to adverse respiratory outcomes. Regarding animal tests, Gerlofs-Nijland et al. (2007) exposed rats to air PM samples and found that they were mostly affected by samples collected at high-traffic sites. They linked adverse effects induced in the lungs and vascular system with specific PM components derived from brake wear (Cu and Ba), tyre wear (Zn), and wood smoke (K). On the other hand, Kreider et al. (2009) and Kreider and Panko (2012) conducted instillation and inhalation studies on rats and concluded that particles generated from the tyre-road interface are unlikely to cause adverse cardiopulmonary effects. They also concluded that tyre wear particles behave like inert particles with respect to inflammogenic potential. Finally, they pointed out that their results indicate that tyre wear particles are less potent inducers of adverse effects compared to other constituents of ambient PM (i.e. diesel exhaust).

Organic constituents of tyre wear debris have also been examined due to their ability to pose adverse health impacts to humans. It is estimated that more than 10% of the tyre debris material is composed of organic compounds. Some organic material can be vaporized leading to highly

carcinogenic volatile compounds such as PAHs (Aatmeeyata et al., 2009; Kwon and Castaldi, 2012). Despite Kreider et al. (2010) found that the total PAHs content of the tread wear particles represent only 5% of the total PAHs content of the road wear particles (<150 μm), the European regulation has already required the discontinuation of the use of high aromatic oil containing PAHs in the manufacture of tyres since 2010 (European Commissions, 2005). Besides PAHs, toxicity tests conducted to *Daphnia magna*, *Pseudokirchneriella subcapitata* and *Ceriodaphnia dubia* showed that tyre particle leachates which have passed through a C18 SPE column were less toxic compared to untreated leachates, thus indicating that toxicity is also caused by non-polar organic compounds (Wik and Dave, 2009). Exposure of human alveolar lung cells (A549) to organic extracts of tyre particles (10-80 μm) caused a dose-dependent increase in cell mortality and DNA damage, as well as significant modification of cell morphology, particularly at higher doses (Gualtieri et al., 2005). Additionally, Gualtieri et al. (2008) linked organic tyre particle extracts (10-80 μm) with the production of reactive oxygen species in human alveolar lung cells. They also concluded that when ROS generation reaches high levels, a general inhibition of protein synthesis probably occurs, culminating in cell toxicity. Finally, the presence of natural rubber latex proteins in tyre wear particles has been connected by some researchers with the increase in latex allergy and asthma mortality (Dorsey et al., 2006), while others mention that the levels of bioavailable natural rubber latex proteins from tyre particles in the air are extremely low to be a significant contributor to these health problems (Finley et al., 2003).

4. CONCLUSIONS

The main conclusions drawn from the present literature study can be summarized to the following points:

- Exhaust and non-exhaust sources contribute almost equally to total traffic-related PM_{10} emissions. Brake, tyre and road wear along with road dust resuspension have been recognized as the most important non-exhaust traffic related sources, with their relative contributions to non-exhaust traffic related emissions ranging between 16-55% (brake wear), 5-30% (tyre wear) and 28-59% (road dust resuspension). Brake wear contribution to traffic-related PM_{10} emissions is much lower in freeways due to significantly reduced number of braking events, while tyre wear contribution is much higher in areas where studded tyres are used. It is predicted that the relative contribution of non-exhaust sources to traffic related emissions (PM_{10} and $\text{PM}_{2.5}$) will increase in the forthcoming years due to stricter control in exhaust emissions.
- It is estimated that approximately 50% of total brake wear and 0.1-10% of tyre wear is emitted as airborne PM_{10} . The rest may deposit on the road or nearby or be attracted by the vehicle. Furthermore the fate of bigger particles has not yet been well investigated.
- Several factors affect both physicochemical characteristics and generation rates of tyre and brake wear particles, making it very difficult to understand the generation mechanisms and study the properties of those particles. Furthermore, there is a wide variety of sampling methodologies (which include a wide range of applied speeds, accelerations and decelerations) which very often result in non-comparable and in some cases even contradictory results.
- Brake wear PM_{10} usually display a unimodal mass size distribution with the peak lying between 2-6 μm . In case of tyre wear PM_{10} some researchers find unimodal and others bimodal size

distributions with one peak lying within the fine mode and the other among coarser particles. In any case, a significant part of tyre and brake wear PM₁₀ lies within the fine size fraction.

- Particle number distributions of brake wear PM₁₀ appear to be bimodal with both peaks lying within the fine mode. Some researchers mention that the first peak lies among ultrafine particles (<100 nm), while others find it at approximately 300-400 nm. In case of tyre wear PM₁₀ most researchers mention unimodal distribution. However, there is no consensus regarding where the peak of the distribution is found.
- The most important chemical constituents of brake and tyre wear in both coarse and fine particle fractions are given in Table 11. Despite the fact that some research regarding organic constituents of wear particles (<200 µm) has been conducted, there is very limited information regarding organic constituents of tyre and brake PM₁₀.

Table 11: Most important chemical constituents of PM₁₀ wear particles in both fine and coarse particle fraction

	PM _{2.5}	PM _{2.5-10}
Brake Wear	Transition metals (Cu, Fe), Sb (III), Sb (V), Sn, Ba, Zr, Al, S, OC>>EC	FeO, Fe₂O₃, Cu oxides, Sb (III), Sb (V), Sn, Ba, Zr, Al
Tyre Wear	Zn, organic Zn, Cu, S, Si, Organic carbon, EC	Zn, organic Zn, Cu, Si, Mn

- Brake and tyre wear PM₁₀ emission factors of 1.0-9.0 mg km⁻¹ vehicle⁻¹ and 4.0-13 mg km⁻¹ vehicle⁻¹ for LDVs, respectively have been reported. Most studies find PM₁₀ EFs of approximately 6.0-7.0 mg km⁻¹ vehicle⁻¹ for both sources, which is very close to the standard for exhaust emissions of Euro 5/6 diesel vehicles. Brake and tyre wear PM₁₀ EFs of HDVs are approximately one order of magnitude higher than of LDVs. Also, much higher PM₁₀ emission factors have been reported when studded tyres are employed. Most commonly used key tracers of brake wear in receptor modeling studies are Cu and Sb. On the other hand, when tyre wear is investigated Zn (which has also several other sources), benzothiazoles and SBR are employed.
- Brake and tyre wear contain particles from all fractions involved in the respiratory function. Additionally, some constituents of airborne brake and tyre wear particles have been recognized as dangerous or potentially dangerous for humans. However, there are no comprehensive studies linking brake or tyre wear particles with adverse effects on human health, while animal and in vitro studies have reached contradictory conclusions.

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