

Jasna Glišović¹⁾
Radivoje Pešić¹⁾
Jovanka Lukić¹⁾
Danijela Miloradović¹⁾

1) University of Kragujevac,
Faculty of Engineering, Serbia
{jaca, pesicr, lukicj,
neja}@kg.ac.rs

AIRBORNE WEAR PARTICLES FROM AUTOMOTIVE BRAKE SYSTEMS: ENVIRONMENTAL AND HEALTH ISSUES

***Abstract:** Road traffic emissions are a major contributor to ambient particulate matter concentrations and therefore, these emissions are targeted through increasingly stringent European emission standards. These legal restrictions succeed in reducing exhaust emissions, but do not address “nonexhaust” emissions from brake wear, tire wear, clutch wear, road surface wear, and corrosion of other vehicle components in air of road dust. Several studies were done to understand the synthesis, composition and distribution of brake dust because of the growing awareness of environmental and health effects, for example, with antimony and copper in the brake pads. This is mainly because of the complex and susceptible characteristics of a brake system and the limitations of many measurement systems. With every change in temperature, braking speed, braking pressure, pad formulation, brake type and history of the friction partner, differences of the properties of brake dust particles will be recognizable. 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 wear.*

***Keywords:** Brake System, Wear Particles, Legal Requirements, Health*

1. INTRODUCTION

Road traffic-related sources have been recognized as a significant contributor of particulate matter especially within major cities. Over the last decades, the automotive industry has made huge efforts to reduce vehicle emissions which resulted in a reduction of emission level in inner city areas. In Europe, limitations for particle emissions from diesel engines have dropped by 97% during the last two decades. In addition, friction materials have undergone many changes and components with an associated health hazard potential have been gradually replaced. Currently, several attempts were made to understand the synthesis, composition and distribution of brake dust because of the growing awareness of environmental and health effects, for example with antimony and copper in the brake pads.

However, with regards to a continuously further concentration of traffic in urban city areas, further measures and legal restrictions are

to be expected. Vehicle homologation registration could in the near future go beyond just emissions from engines to address total vehicle emissions. This would make the contribution from tires, clutch, and road surfaces together with brake friction pads and discs a part of the overall balance [1].

In Europe and US ambient air quality standards have been developed or are under discussion as concerns novel issues. The Environmental Agencies and WHO are reporting exceeded limits of air pollutants and their increasing effects on human health and environment. In Europe, the effects of poor air quality have been felt the most in urban areas, where the majority of the European population lives, leading to adverse effects on public health and on ecosystems, where the pressures of air pollution impairs vegetation growth and harms biodiversity. Human health is the most vulnerable sector and many reports are showing a negative impact of air pollution on respiratory or cardiovascular morbidity, cancer, increased

hospital admissions and even increased rate of death. Generally, brake pads have a complex composition containing even more than 30 different components, some of them more hazardous to health than others. The extent of such emissions depends on their physical and chemical properties and on the tribological interactions with the counter face disc during the braking stages. The most ongoing research analyzes the potential impact of the emitted PM on the human health, depending on the mechanisms of formation and toxicity of the particles [2].

The published measurements for the number and size of brake particles vary widely. Major reason for this is the complex and susceptible characteristics of a brake system and the limited resolution of many measurement systems. With every change in temperature, braking speed, braking pressure, pad formulation, brake type and history of the friction partner, differences in the properties of brake dust particles will be recognizable. One approach to measure the size of the particles is to analyze a sample of collected brake dust in a scanning electron microscope [3]. This means that it is important to focus on influences to and potential reductions of primary brake emissions, not taking into account any secondary means to collect already released brake particles and prevent them from entering the environment. A multitude of tests are usually run on a brake dynamometer and it is able to deliver results in a known environment of realistic driving. The results show a variety of dependencies for brake wear and emissions from the friction pads' materials concepts and the related brake rotors. They also open the view to relations of emissions under various braking conditions [1].

The aim of the present paper is to present the state-of-the-art of the different aspects regarding PM resulting from brake wear and provide all the necessary information in terms of importance, physicochemical characteristics, emission factors and possible adverse health effects.

2. IMPORTANCE OF BRAKE WEAR PARTICLES

Two brake system configurations have been widely used in modern passenger vehicles: disc brakes, in which flat brake pads are forced against a rotating metal disc (Fig. 1), and drum

brakes, in which curved brake shoes are forced against the inner surface of a rotating drum. Modern passenger vehicles are usually equipped with disc front and rear brakes, while in the past, drum brakes were usually employed as rear brakes. It is estimated that front brakes have to provide approximately 70% of total braking power and therefore have to be replaced more frequently than rear ones [4].

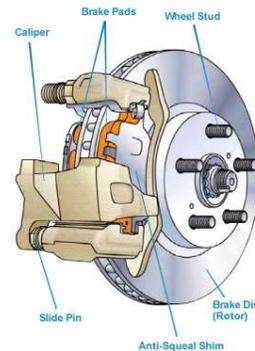


Figure 1. Graphic representation of a disc brake system

The majority of car braking systems consist of frictional pairs made of a disc, a pad and a calliper. Figure 1 depicts a disc brake assembly with a single-piston floating calliper and a ventilated rotor. Rotors used in passenger vehicles are usually made of grey cast iron, but in some cases, they can be made of composites such as reinforced carbon-carbon, ceramic matrix composites and aluminum. Brake linings generally comprise five main components: binders, fibres, fillers, frictional additives or lubricants and abrasives. Binders hold the components of the brake pad together and ensure the structural integrity of the lining under mechanical and thermal stress. Various modified phenol-formaldehyde resins are used as the binders. Fibres can be classified as metallic, mineral, ceramic, or aramide, and include steel, copper, brass, potassium titanate, glass, asbestos, organic material, and Kevlar. Fillers tend to be low-cost materials such as barium and antimony sulphate, kaolinite clays, magnesium and chromium oxides, and metal powders. Friction modifiers can be of inorganic, organic, or metallic composition. Graphite is a major modifier used to influence friction, but other modifiers include cashew dust, ground rubber, and carbon black. Abrasives are used in order to increase friction, maintain cleanliness between

contact surfaces and limit the buildup of transfer films. Aluminum oxide, iron oxides, quartz and zircon are the most common abrasive constituents. Three different brake lining types are usually found in passenger vehicles: non-asbestos organic (NAO), semimetallic and low metallic (LM). Modern asbestos-free brake linings contain different inorganic compounds to older linings, though the metal compounds have remained more or less the same. The metal contents of brakes are presented in Table 1. The results show that significant amounts of copper (up to 1.4% by mass) and iron (up to 4% by mass) can be present. Other metals, notably calcium, sodium, and zinc, are also prominent [5].

Table 1 - Metal content of brakes

| Metal | Concentration range (mg/kg) | Metal | Concentration range (mg/kg) |
|-------|-----------------------------|-------|-----------------------------|
| As | 10 | Mn | 3,220 |
| Al | 3,770 | Mo | 10,000 |
| Ba | 2,640 | Na | 15,400 |
| Ca | 14,300 | Ni | 210-850 |
| Cd | 2.7-29.9 | Pb | 1,960-3,900 |
| Co | 6.43 | Sb | 10,000 |
| Cr | 162-1,200 | Se | 20 |
| Cu | 15,100-142,000 | Sn | 7,000 |
| Fe | 115,000-399,000 | Sr | 81.4-740 |
| K | 857 | Ti | 3,600 |
| Mg | 6,140 | V | 660 |
| Li | 55.6 | Zn | 270-21,800 |

NAO-type pads are relatively soft and exhibit low brake noise compared to other types of pads, but they lose braking capacity at high temperature and create more dust than the other types. Low-metallic pads comprise organic compounds mixed with small amounts of metals (10–30 % by mass). They exhibit high friction and good braking capacity at high temperatures. Semimetallic brake pads have higher metallic content (up to 65% by mass), which makes them more durable and with excellent heat transfer. On the other hand, they tend to wear down rotors faster and exhibit intrusive noise characteristics. For high performance requirements, or extreme braking conditions (sports cars, ambulances, police cars), metallic linings which contain steel and copper fibres are employed.

The frictional contact between the disc and the pad generates particles of various sizes. During a braking event, the calliper acts mechanically on the pad, which slides against the disc and transforms vehicle kinetic energy

into thermal energy. Apart from themechanical abrasion, vehicle brakes become subject to large frictional heat generation with subsequent wear of linings and rotors. This generates mostly micron-sized particles [4].

Particulate matter (PM) is made up of solid or liquid particles suspended in a gas or liquid and atmospheric aerosols refer to the particles and gas together. The aerodynamic diameter is the diameter of a sphere of unit density that has the same gravitational settling velocity as the particle in question. Particles with an aerodynamic diameter less than 10 µm (PM₁₀) are divided into a coarse fraction (>1 µm), a fine fraction (<1 µm, PM₁), and an ultrafine fraction (<0.1 µm, PM_{0.1}). Figure 2 presents typical size distributions of atmospheric particulate matter with the size classification marked [6].

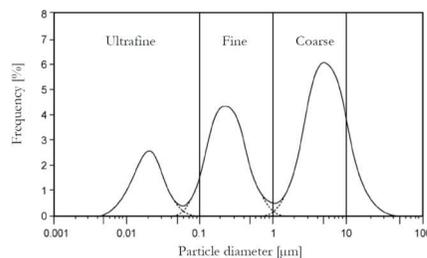


Figure 2. Typical size distribution of atmospheric particulate matter with the size classifications marked [6]

Since the end of the last century EU legislation focused on solid emissions in the form of particulate matter (PM) besides such in gaseous form like carbon dioxide. The contribution of road transport (including resuspension) to PM is identified as the most important, according to the German Umweltbundesamt (Figure 3).

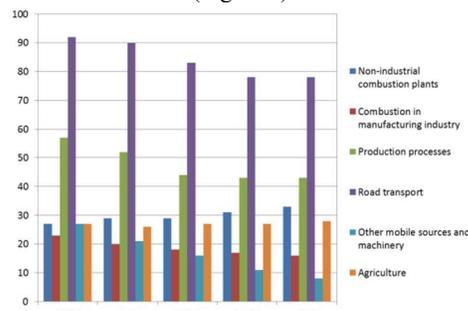


Figure 3. PM₁₀ Emissions in Germany and related sources [7]

As a consequence, the automotive industry has undertaken significant measures to reduce emissions from combustion engines, whereas emissions related to brake and tyre wear are remaining on a constant level (Figure 4).

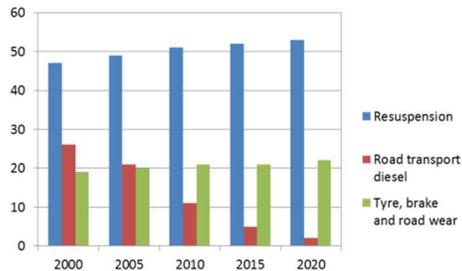


Figure 4. PM₁₀ emissions from road transport

A preliminary report of the German Environmental Agency presents an estimation for 2015 naming emissions in PM₁₀ (particles with an aerodynamic diameter smaller than 10 μm) of 21 Gg from road transport in case of tire and brake wear per anno, compared to a contribution of 5 Gg from diesel engine emissions and 50 Gg caused by resuspension from roads. With the ongoing process to reduce fine and ultrafine dust emissions “wear-born” PM will be in the focus over the next years [7].

3. BRAKE WEAR PARTICLES AND THEIR EFFECTS ON HUMAN HEALTH

The controlling factors in the sizes and morphologies of these particles are first, wear modes (i.e. adhesion, fatigue, delamination and thermal degradation): for example, sheet-like particles imply delamination and fatigue; small aspect ratios imply abrasion [8]. Second, the braking style (i.e. the pressure and duration of the contact) is a factor. Agglomeration and fragmentation occur concurrently, and the particle composition, by virtue of frictional heating and consequent tribochemical reactions, can differ from that of the progenitor material.

Several demographic characterisations of brake-wear particles, given in Figure 5, show accumulation modes (350 nm) and coarse modes (2–15 μm) [8]. Two aspects of these data are intriguing. First, coarse-mode particle sizes are strong functions of braking style; indeed, continuous braking and high contact pressures seemed to facilitate growth or, rather, to favour

agglomeration over fragmentation. The accumulation modes, by contrast, were relatively indifferent to braking style. Secondly, accumulation modes are unexpected, insofar as these do not, like coarse modes – according to classical notions of aerosols, that is – stem from material disintegration. Conjecturally, frictional heating brought about decomposition, and the resulting emission of some unknown vapour, the nucleation of which formed nanoparticles, and the agglomeration of which formed the accumulation modes. Measurements of particle composition pointed to the brake pad as the parent material for these accumulation modes [9].

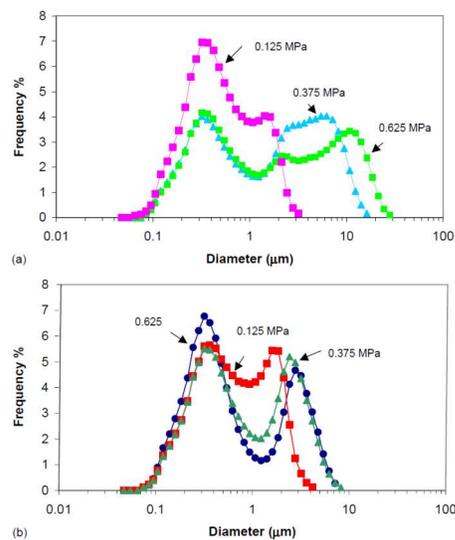


Figure 5. Size distribution of wear particles generated during (a) low-speed, continuous tests (b) low-speed, discontinuous tests [8].

Inhaled PM₁₀ are deposited in the nose and throat, causing irritations, while fine and ultrafine particles may penetrate deep into the lungs, causing inflammation, create free radicals in the body cells and produce damage to DNA, especially for oxidation reactions and related biological stress.

Several studies proved that the nanosized particles may become blood-borne and be transported to other target tissues and organs, like liver, kidneys, and brain. Nanoparticles enter human body through the skin, lung and gastrointestinal tract. PM_{2.5} penetrates into the small airways and air exchange regions of the

lungs. Because of their very small size, nanoparticles can penetrate deeper into the lungs and enter the pulmonary interstitial and vascular space, to be subsequently absorbed directly into the blood stream. Nanoparticles have a large surface area and that makes them more reactive and toxic, thus increasing their detrimental health effects, like pulmonary inflammation and cardiovascular events. They may also move within the body to the central nervous system, the brain, into the systemic circulation and other organs like the already mentioned liver.

Metals present in brake wear particles, like iron, copper, manganese, etc., may damage the lung cells tight junctions with a mechanism involving oxidative stress and increase of inflammatory responses.

Brake linings have a complex chemical composition which varies a lot in relation with the manufactures, or depending on certain types of brakes. Nevertheless, copper and antimony are considered as fingerprints for brake wear particles. Studies performed in Germany and Netherlands at different locations revealed, an enrichments of these two elements, attributed to brake wear emissions. Netherlands Emission Inventory published a review on road traffic brake wear emissions, based on a number of studies available on brake wear particulate matters. It was concluded that the most important metal pollutants, as concerns scope and toxicity, are Cu, Cd, Ni, Pb, Sb and Zn.

One of the most commonly reported adverse health effect of copper is gastrointestinal distress. Copper is also irritating to the respiratory tract. The liver and kidney are also sensitive targets of toxicity. A number of studies report eye irritation, whereas inhalation can result in irritation of nasal mucosa membranes, indirect eye irritation, upper respiratory tract irritation; metallic taste, headache. The liver and kidneys are sensitive targets of copper toxicity. In fact, acute copper poisoning can cause liver injury, methemoglobinemia and hemolytic anaemia, dizziness, vomiting and diarrhoea, tachycardia, respiratory difficulty, hemolytic anaemia, liver and kidney failure, and even death [2].

4. LEGAL REQUIREMENTS

The EU funded REBRAKE project is one of the many international research projects that are tackling the problem of wear debris

emissions from brakes. The main task of the international REBRAKE is the development of new materials and systems capable to achieve a 50% reduction in the emission of PM from automotive brakes. One of the leading action of the Project is to achieve a deep understanding of wear mechanisms, that are of course fundamental for an effective and safe braking, although are even the first responsible for the production of debris, contributing to the overall PM concentration in the atmosphere. The study of the wear mechanisms is strongly relying on the characterization of the wear products, in particular wear tracks and debris [2].

Knowing the influencing factors on brake dust emissions and how to measure the impact of changed parameters, it is possible to systematically search for measures to reduce the particle emission. This can be done in different ways on the brake e.g. change in formulation, collect the particles or change their physical properties in a way that makes then less harmful. As mentioned before, the change in formulation of pads or even disc is possible but immense difficult with a time-costing way to solve several conflicts of aims. One possible low-emission design measures with collector was already tested on the brake test bench at the TU Ilmenau. As already mentioned, the fine dust tends to follow any air stream, so it is feasible to install a collector with additional tubing and air ventilation to guide the particles into a filter medium. Experiments on the dynamometer showed a significant high reduction of particle emission outside the wheel hub [10].

Since the phase out of asbestos brakes, brake lining material contains 1–14% Cu with an average Cu content of 5–10% in current brake linings. This makes brake wear from vehicles an important source of atmospheric (particulate) copper concentrations. It is the dominating source of copper in ambient air in Western Europe [11].

The history of changing regulations governing chemical compounds used in automotive brake pads in North America is shown in Figure 6. Conversely, brake pads capable of suppressing vibration and offering reduced drag resistance to limit brake squeal and boost fuel efficiency are required [12].

In March 2010, Washington became the first state to pass legislation in an effort to protect its waterways from the runoff of toxic copper brake dust. California also passed a bill,

which became law in September 2010. Similar legislation is underway in other states.

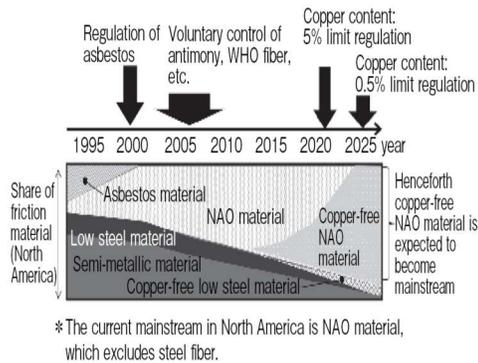


Figure 6. Change in the Regulation of Chemical Substances for Brake Pads [12]

The California law mandates that brakes contain no more than 5 percent copper beginning in 2021. By 2025, the limit will be reduced to 0.5 percent. Washington’s law is similar, with a 5 percent limit by 2021, and the establishment of an advisory committee to assess the feasibility of lowering the limit to 0.5 percent in subsequent years.

5. CONCLUSION

The present paper has highlighted the role played by wear debris and fragments coming from automotive brake systems in the PM production and emission in the atmosphere.

Exhaust and non-exhaust sources contribute almost equally to total traffic-related PM₁₀ emissions. Brake wear has been recognized as one of the most important non-exhaust traffic-related source, with its relative contribution to nonexhaust traffic-related emissions ranging between 16 and 55 % and to total traffic-related PM₁₀ emissions between 11 and 21 %. It is estimated that approximately 50% of total brake wear is emitted as airborne PM₁₀. The rest may deposit on the road or nearby or maybe attracted by the vehicle. The fate of bigger particles has not yet been well investigated. Brake wear contains particles from all fractions involved in the respiratory function. Additionally, some constituents of airborne brake wear particles have been recognized as dangerous or potentially dangerous for the human health. However, there are no comprehensive studies linking brake wear particles with adverse effects on human health, while it is difficult to extrapolate animal and in vitro studies to humans.

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