

AQUATIC TOXICITY OF AIRBORNE BRAKE WEAR PARTICLES TO *RAPHIDOCELIS SUBCAPITATA*

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Abstract

Wear debris from automotive brake systems represents a major source of non-exhaust emissions from road traffic. Amount of brake wear debris released to the environment increased with numbers of cars. However, their impact on the environment and human health is still unknown. One of the ways how to evaluate their potential environmental impact is testing the acute aquatic toxicity on freshwater green algae.

Aim of this study is evaluation of the acute aquatic toxicity of airborne brake wear debris particles on freshwater green algae *Raphidocelis subcapitata*. Elemental composition of collected brake wear debris after standard dynamometer test was analyzed by scanning electron microscopy and X-ray fluorescence analysis and phase composition was determined by X-ray powder diffraction analysis. Particle size distribution was characterized, as well. Airborne brake wear debris contains particles in the range values from 3.98 μm (d_{10}) to the 75.18 μm (d_{90}) and its composition is mostly based on amorphous carbon and iron. Accumulation of these elements and compounds in the environment may pose risk to the water environment. The fifty percent effective concentration (EC_{50}) was determined for the concentration 50.73 g/l of airborne brake wear debris to freshwater green algae *Raphidocelis subcapitata*

Keywords: Brake wear debris, acute aquatic toxicity, *Raphidocelis subcapitata*

1. INTRODUCTION

Braking is an important source of particle emissions originated from automotive braking processes and may pose negative impact to the environment and living organisms [1]. Amount of brake wear particles released to the environment is closely related to the number of cars worldwide. Friction materials for brake linings usually consist of more than 10 components [2], including phenolic binders, abrasives, lubricants, and fillers [3]. High pressure and temperature during braking process affect size, properties, and chemical composition of formed emitted particles [4], typically metal oxides and degradation products of phenolic resin. Brake wear particles are produced in two fractions: airborne particles are released into the air and nonairborne particles are deposited on surface of road and automobile hardware [5]. Garg *et al.* reported that 35 % of brake wear debris is emitted as airborne fraction, which total amount of released particles was determined to 11 mg/km [6].

Several toxicological studies suggested that brake wear debris can negatively influence living organisms and their parts. Peikertová *et al.* determined that airborne fraction shows relatively low toxicity (EC_{50} 85.46 g/l) to green algae *Raphidocelis subcapitata* [7]. Dodd *et al.* found out, that brake wear debris may cause decrease of germination and root elongation of lettuce (*Lactuca sativa*) and wheat (*Triticum aestivum*) [8]. On the contrary Shupert *et al.* observed growth stimulation of *Salvinia molesta* cultivated in extract of low metallic brake wear debris [9]. According to Kazimirova *et al.* airborne brake wear debris from low metallic brakes can caused damage of chromosomes and may be responsible for genotoxicity [10]. Malachová *et al.* proved acute toxicity of nonairborne particles from low metallic brake pad to *Vibrio fischeri* [11]. Toxicological studies have suggested that brake wear debris, especially metallic, may damage organisms within the mechanism that

involve oxidative stress and proinflammatory reaction [12]. Our experience shows that airborne particles are able to induce oxidative stress via protein carbonylation.

Aim of the study was to characterize collected airborne brake wear debris after standard dynamometer test and evaluation of the acute aquatic toxicity to freshwater green algae *Raphidocelis subcapitata*. Sample was characterized by scanning electron microscopy (SEM/EDS), X-ray fluorescence spectroscopy (XRFS) and X-ray powder diffraction (XRPD) to determine morphology, phase and elemental composition and dynamic light scattering to determine the particle size distribution (PSD).

2. EXPERIMENTAL

2.1. Brake wear debris generation

For generation of brake wear debris automotive full scale brake dynamometer model M2800 (LINK Engineering) was used. Brake wear debris was collected after standard dynamometer tests from filter (KS 85 Klima - Service, a.s., Czech Republic) located in dynamometer ventilation system. Tested material contains particles from different low metallic brake pads and simulates real traffic emissions.

2.2. Analytical methods

Experimental data on morphology and elemental composition of studied materials were obtained from scanning electron microscope (SEM) (Philips XL-30) equipped with EDS (EDAX) detector. Samples were attached on the carbon conductive tape for the SEM analysis.

An energy dispersive XRFS spectrometer SPECTRO XEPOS (SPECTRO A. I., Kleve, Germany) was used for elemental analysis. For samples excitation 50 W Pd end-window tube operating at max. 50 kV is used. The target changer, with up to 8 polarization and secondary targets, offers many various excitation conditions ensuring optimum determination of all elements from Na to U. Measurements were performed in He atmosphere. Silicon drift detector with Peltier cooling achieves a spectral resolution of less than 160 eV for Mn K- α , the maximum count rate is 120 kcps. Special SPECTRO TurboQuant method for powders was used for the measurement of wear debris from automotive brake system.

Total carbon (TC) content was determined by HT 1300 Solids (Analytic Jena AG, Germany) with analyzer Multi N/C 3100.

The XRPD patterns were recorded under CoK α irradiation ($\lambda = 1.789 \text{ \AA}$) using the Bruker D8 Advance diffractometer (Bruker AXS) equipped with a fast position sensitive detector VÅNTEC 1. Measurements were carried out in the reflection mode, powder samples were pressed in a rotational holder, goniometer with the Bragg-Brentano geometry in 2θ range from 5 to 80°, step size 0.03°. Phase composition was evaluated using database PDF 2 Release 2014 (International Centre for Diffraction Data).

The particle size distribution (PSD) was determined by using laser diffraction particle size analyser (HORIBA LA-950 instrument). Before measuring the sample was sonicated in water solution with one drop of detergent for 45 s. The PSD analyses were conducted with the refractive index 2.900 for airborne brake wear debris and 1.333 for water suspension. Results were output as the volume PSD. Each data point is an average of approximately 5 measurements.

2.3. Leachate preparation

For leachate preparation 15 g of brake wear debris in 150 ml of distilled water were used. This solution was stirred in an orbital shaker for 24 h. Obtained solution was filtered per vacuum filtration apparatus with membrane filter Pragopor 6 (pore size 0.4 μm).

2.4. Acute aquatic toxicity test

For performance of acute aquatic toxicity test on freshwater green algae were used: *Raphidocelis subcapitata* (CCALA, Institute of Botany of the Academy of Sciences of the Czech Republic in Třeboň). Acute aquatic toxicity tests were done according to the ČSN EN ISO 8692 Standard [12]. For algae cultivation 2x6 Erlenmeyer flasks (volume 100 ml) was filled by 25 ml of solution, which contains algae suspension (3 days old) in concentration 10 000 cells/ml, salts for enrichment of leachate (solution was prepared according to the standard ČSN EN ISO 8692) [12], and leachate of the airborne brake wear debris. Concentration range (weight of wear debris particles/volume of distilled water) for determining of EC₅₀: 100 g/l, 80 g/l, 60g/l, 40 g/l, 20 g/l, and 0 g/l. Erlenmeyer flasks were placed in thermo box (T=23 ± 2 °C) with continuous illumination and after 72 h cultivation the cell density was determined.

3. RESULTS AND DISCUSSION

3.1. Characterization of tested material

Selected image from SEM analysis of airborne brake wear debris (see **Figure 1**) shows heterogeneous aggregates in terms of different morphology, size, and shape. Tested material includes spherical, plated, and sharp edged particles. Spherical particles are typically created during high-temperature processes, sharp edged and plated particles are mostly connected with mechanical wear [1]. EDS analysis was also performed on this sample and results show that the sample is predominantly formed of C, Fe, and O and to a lesser extent other elements such as Zn, Cu, Mg, Al, Si, Ti, etc. (see **Figure 1**). All detected elements commonly occur in initial brake pad formulations and as well in brake wear debris [14]. Presence of oxygen in the EDS record suggests that the oxide forms of the metals are predominantly present in the sample.

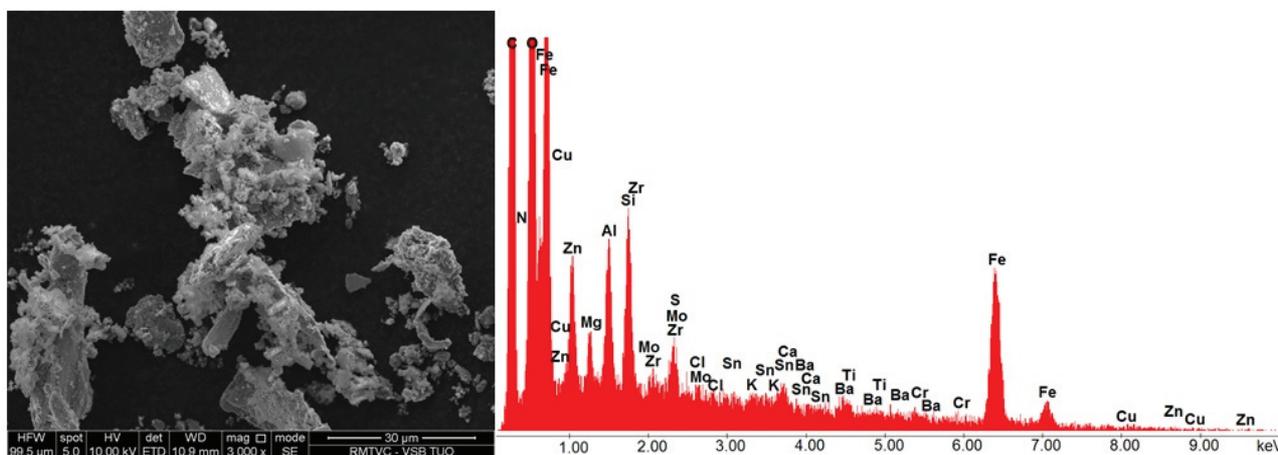


Figure 1 Selected SEM image of airborne brake wear debris

Elemental analysis was also determined by XRFs, which as well confirmed that airborne wear particles have multicomponent composition. The main elements detected in the sample were carbon 28 % wt. (determined by TC analysis) and Fe 49.58 % wt. Other elements had a significantly lower proportion Si 3.08 % wt., Al 2.7 % wt., Mg 1.59 % wt., Zn 1.58 % wt., S 1.04 % wt., Zr 0.74 % wt., Ti 0.62 % wt., Ca 0.6 % wt., Ba 0.55 % wt., and K, Cr, Mn, Ni, Cu, As, Sr, Mo, Cd, Sn, Sb, and Pb below 0.5 wt %/ all about 10 % wt. Mainly detected elements from airborne brake wear particles reported in literature are C, Fe, Cu, Ba, and Pb, but differ considerably [15] according different authors and/or studied brake pads. Elemental composition detected by XRFs is in very good accordance to SEM/EDS analysis of the sample for elements with presence higher than 0.5 % wt.

Phase analysis was determined by XRPD (see **Figure 2**). The results show, that C in the form of graphite, metallic Fe and Cu, iron oxides (FeO, Fe₂O₃, Fe₃O₄), FeS₂, CuZn, and CuSn are major phases formed the sample. Phase composition of brake wear particles may differ from the original friction material, because effect of high pressures and temperatures in presence of O₂, which may lead to the formation of new products (for example oxidation of metallic component mainly cooper and iron) [17]. Unfortunately, verifying of the initial and final phase is impossible due to the know-how of the brake manufacturers. Detected compounds are in accordance to main elements detected by XRFs and SEM/EDS.

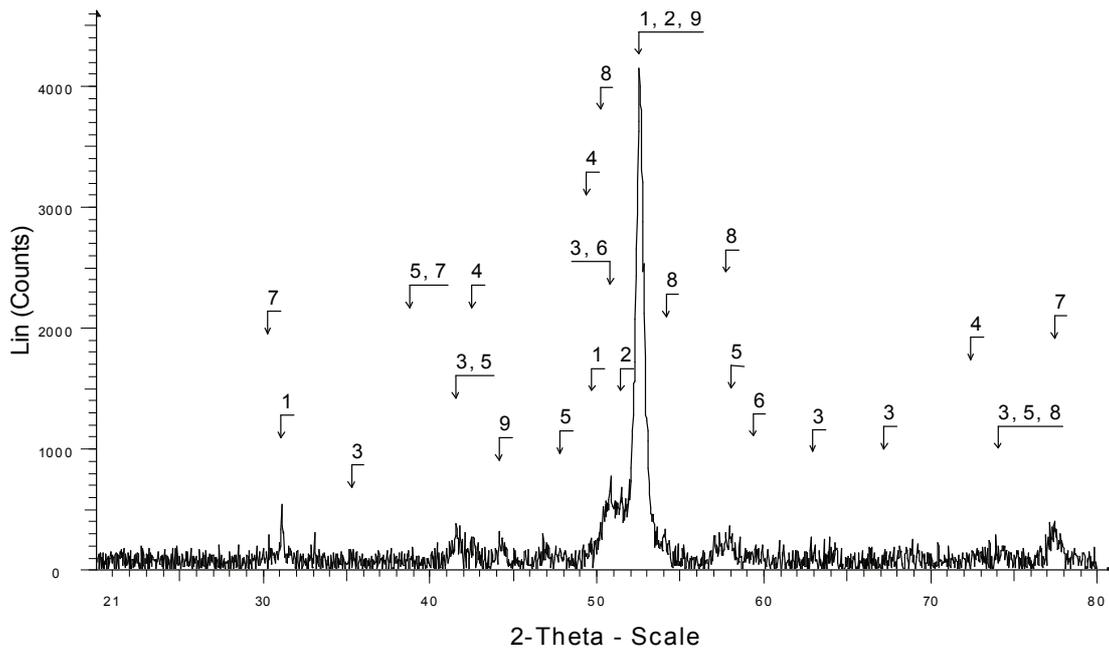


Figure 2 XRPD pattern of airborne brake wear debris (1 - C, 2 - Fe, 3 - Fe₃O₄, 4 - FeO, 5 - Fe₂O₃, 6 - Cu, 7 - FeS₂, 8 - CuZn, 9 - CuSn)

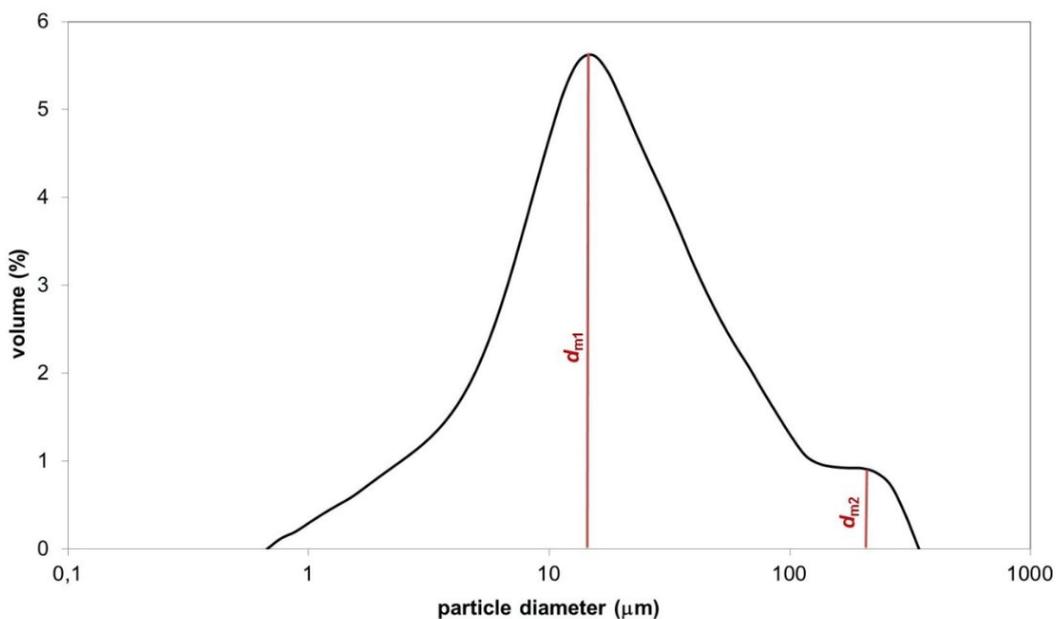


Figure 3 Log-normal particle size distribution of the brake wear debris airborne sample

PSD (volume distribution) of the airborne brake wear debris is shown in **Figure 3**. The mode diameter (dm) and the d_{10} and d_{90} diameters were used for evaluated the particle sizes and the PSD width. The PSD has very broad character with interval values 3.98 - 75.18 μm (d_{10} - d_{90}). Bimodal PSD with two peaks at 15.17 μm (dm_1) and 174.62 μm (dm_2) contributed to the existence of two particle size fractions. The PS values agree with the results from scanning electron microscopy (see **Figure 1**), where dm_2 values correspond with the bigger plated-like particles in the sample volume and as well may be connected with agglomerates. These agglomerates can contain also nanosized particles which can be easily released for example to the water environment [16]

3.2. Acute aquatic toxicity on freshwater green algae *Raphidocelis subcapitata*

In **Figure 4** are shown biomass growth inhibition curves for both experiments. The effective concentration of toxicity (parameter EC_{50}) of brake wear debris leachate to *Raphidocelis subcapitata* was determined as average value from both experiments and its value is 50.73 ± 2.75 g/l. As compared with study of Peikertová *et al.* who determined EC_{50} for airborne brake wear debris to *Raphidocelis subcapitata* to 85.46 g/l [7] ours determined concentration is lower, thus our sample shows higher potential risk still shows no acute aquatic toxicity (material exhibits aquatic toxicity if $EC_{50} \leq 1.00$ g/l) [18]. Due to increasing numbers of cars and possible accumulation of brake wear debris in the environment should be this material considered as potentially dangerous for the environment, including the aquatic ecosystem.

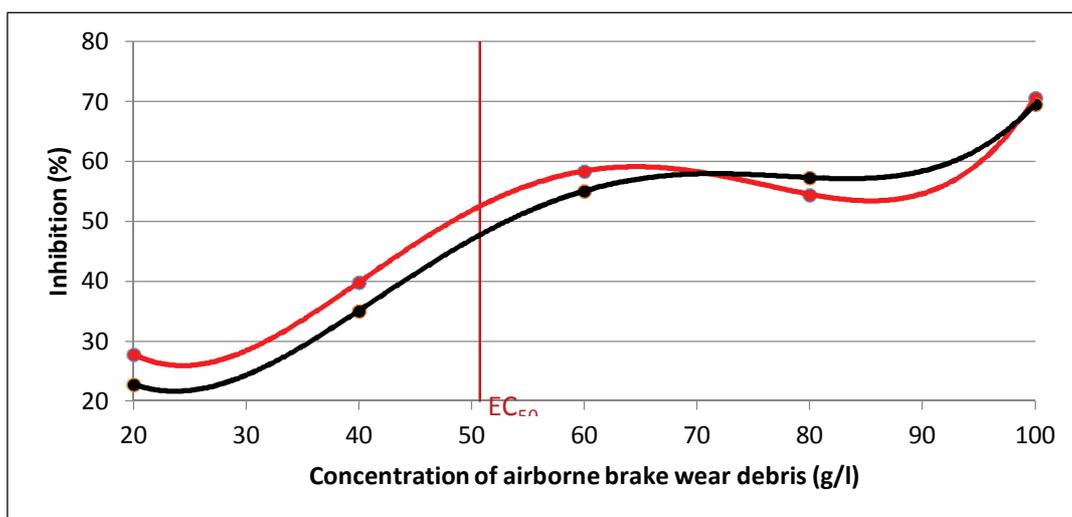


Figure 4 Biomass growth inhibition curve of airborne brake wear debris (EC_{50} is reported as mean of two measurements)

4. CONCLUSION

Collected brake wear debris was deeply characterized by SEM/EDS, XRFs, XRPD, and PSD. Used analytical techniques correspond to each other and proved that the brake wear debris is heterogeneous material with particles of different morphologies, sizes and compositions. Performed acute aquatic toxicity test on green freshwater algae *Raphidocellis subcapitata* show potential to decrease its growth, but show no acute toxicity (EC_{50} - 50.73 ± 2.75 g/l). However, increasing of the brake emissions and their long term accumulation may pose risk to the environment, especially to the water environment.

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