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Elemental composition of current automotive braking materials and derived air emission factors

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HIGHLIGHTS

- Brake wear important source of copper, iron and antimony.
- Brake material analysis supports new emission factors for metals.
- Brake discs and brake pads both contribute significantly to wear emissions.
- Basic tracer information for source apportionment studies.

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ABSTRACT

Wear-related PM emissions are an important constituent of total PM emissions from road transport. Due to ongoing (further) exhaust emission reduction wear emissions may become the dominant PM source from road transport in the near future. The chemical composition of the wear emissions is crucial information to assess the potential health relevance of these PM emissions. Here we provide an elemental composition profile of brake wear emissions as used in the Netherlands in 2012. In total, 65 spent brake pads and 15 brake discs were collected in car maintenance shops from in-use personal cars vehicles and analyzed with XRF for their metal composition (Fe, Cu, Zn, Sn, Al, Si, Zr, Ti, Sb, Cr, Mo, Mn, V, Ni, Bi, W, P, Pb and Co). Since car, engine and safety regulations are not nationally determined but controlled by European legislation the resulting profiles will be representative for the European personal car fleet. The brake pads contained Fe and Cu as the dominant metals but their ratio varied considerably, other relatively important metals were Sn, Zn and Sb. Overall a rather robust picture emerged with Fe, Cu, Zn and Sn together making up about 80–90% of the metals present in brake pads. Because the XRF did not give information on the contents of other material such as carbon, oxygen and sulphur, a representative selection of 9 brake pads was further analyzed by ICP-MS and a carbon and sulphur analyzer. The brake pads contained about 50% of non-metal material (26% C, 3% S and the remainder mostly oxygen and some magnesium). Based on our measurements, the average brake pad profile contained 20% Fe, 10% Cu, 4% Zn and 3% Sn as the dominant metals. The brake discs consisted almost entirely of metal with iron being the dominant metal (>95%) and only traces of other metals (<1% for individual metals). Non-metal components in the discs were 2–3% Silicon and, according to literature, ~3% carbon. The robust ratio between Fe and Cu as found on kerbsides has been used to estimate the contribution of brake pads and brake discs to total brake wear. Based on this approach our hypothesis is that 70% of the brake wear originates from the discs and only 30% from the brake pads.

1. Introduction

Road transport particulate matter (PM) emissions consist of engine exhaust emissions and non-exhaust emissions. While engine exhaust emissions have been strongly reduced by EU emission standards in the past decades, non-exhaust emissions are unaffected by such measures and become more and more (health) relevant (Denier van der Gon et al., 2013). Non-exhaust emissions originate from brake wear, road wear, tyre wear and road dust resuspension. These "non-exhaust" sources contribute easily as much as the tailpipe exhaust to the ambient air PM concentrations in cities, and their relative contribution to ambient PM burden is

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destined to increase in the future, posing obvious research and policy challenges (Denier van der Gon et al., 2013; Amato et al., 2014). Rexeis and Hausberger (2009) even estimated that around 2020 nearly 90 percent of emissions from road traffic will come from non-exhaust sources. A recent study in the Netherlands (Hulskotte and Jonkers, 2012) confirmed that road transport exhaust and wear related PM10 emissions are presently of the same order of magnitude and that wear emissions become a dominant source by 2020.

Wear emissions and especially brake wear contains several chemical components, including (heavy) metals, that potentially contribute significantly to the adverse health effects related to road transport particulate matter emissions (Riediker et al., 2004; Perrenoud et al., 2010; Denier van der Gon et al., 2013). Recently Pant and Harrison (2013) reviewed the road traffic contribution to particulate matter concentrations, including the contribution of brake wear, and found very different ratios between metals in the environment such as the Cu:Sb-ratio. Pant and Harrison (2013) conclude that differences in the brake pad composition and contribution of other sources may be the main reasons for these observed differences. Clearly, a well-balanced assessment of the chemical composition of brake wear materials is crucial for a proper understanding of its health relevance.

1.1. Brake pad formulations from literature

From the literature it is known that a very broad spectrum of brake pad formulations are used in practice (Chan and Stachowiak, 2004). According to Filip et al. (1997) brake pad linings are complex composites typically formulated of more than 10 constituents, and more than 3000 different materials are used in different brands. Another reference that is giving more detailed information on the huge variation in formulations is Blau (2001).

Sanders et al. (2003) and den Hoed (2010) discriminate between three type of brake linings: NAO (non-asbestos organic), semi-metallic and low-metallic. According to these authors low-metallic brake linings are currently dominantly used in Europe. According to Sanders and den Hoed low-metallic brake linings compared to NAO exhibit higher levels of wear debris and of this debris a larger portion consists of iron.

In a recent investigation on an unknown number of European brake pads Kukutschová et al. (2011) observed by polarized light microscopy constituents like iron powder, brass chips (CuZn), Cu-powder, steel chips, petroleum coke and graphite and butadiene rubber. In X-ray diffraction spectra several other constituents could be recognized: low carbon steel (Fe), graphite, copper, sulphides (SnS, ZnS, MoS_2), periclase (MgO) and zircon ($ZrSiO_4$). In addition, chemical analysis revealed smaller amounts (lower than 0.1 wt%) of mercury (Hg), antimony (Sb), barium (Ba) and nickel (Ni) (Kukutschová et al., 2011).

With many possible formulations which are all proprietary information of private companies there seems to be only a single way of retrieving a representative picture of the elemental composition of brake materials: collect and analyze as many samples that can be obtained and analyzed.

The objective of this research was to obtain a more representative picture of the chemical composition of braking materials from personal cars that currently are on the road in the Netherlands. This article presents the results of an investigation of the elemental composition of braking materials that recently were used in several types of cars in the Netherlands. Used brake pads and brake discs from personal cars were collected at 6 car maintenance facilities and consequently analyzed by XRF-analysis and partly also by ICP-MS.

2. Materials and methods

2.1. Collecting of the brake materials

In the period between June and November 2012 spent friction materials from in-use personal cars were collected at 6 car repair shops at several locations spread over the Netherlands (Utrecht (4), Nijkerk (1) and Arnhem (1)). The friction materials that were collected consisted of 65 brake pads and 15 brake discs from 8 very common car brands in Europe including Volkswagen, Opel, Ford, Citroen, Peugeot, Fiat, Volvo and Mazda. Theoretically, the composition of spent braking materials may be (slightly) different from new braking materials. Our intention, however, was to obtain actual in-use materials and no new materials were analyzed.

In a plastic box a sufficient amount of sealable plastic bags were available to put in the spent brake pads (Fig. 1). However in most cases the mechanics put the spent parts in the boxes of the replacing new parts. The shop mechanics were asked to fill in a form with characteristics of the collected materials such as brand and car-model and front or rear mounted parts. In some cases the mechanics placed a copy of the work order in the box to serve as background information. An overview of collected materials and analytical methods applied to the samples is presented in Table 1.

2.2. Chemical analysis

All brake pads and discs were analyzed by handheld XRF (X-ray fluorescence). XRF has the advantage that it enables the analysis of a large number of samples without the labor intensive and costly job of destructing the brake materials. A disadvantage of the mode wherein the XRF-instrument was operated is that it only delivers metal percentages relative to the total amount of elements that was analyzed. Since XRF cannot measure elements like C, N, and O, S delivered inconsistent results and the instrument was not calibrated for Mg and Ba, the percentages of metals are not representative for the absolute percentage of each metal in a brake pad. This disadvantage could (partly) be canceled by additional ICP-MS and total carbon and sulphur analysis on a selection of nine brake pads. Ideally, all collected pads would have been analyzed by ICP-MS but this was too costly and labor intensive.

XRF is a technique which uses the emission of fluorescence from materials after ionization with high-energy X-rays. The intensity of the characteristic fluorescence depends on the content of the element, but also on the matrix of the sample. In order to correctly interpret the signals, calibration with similar materials with known element contents is necessary. The depth of penetration of the X-

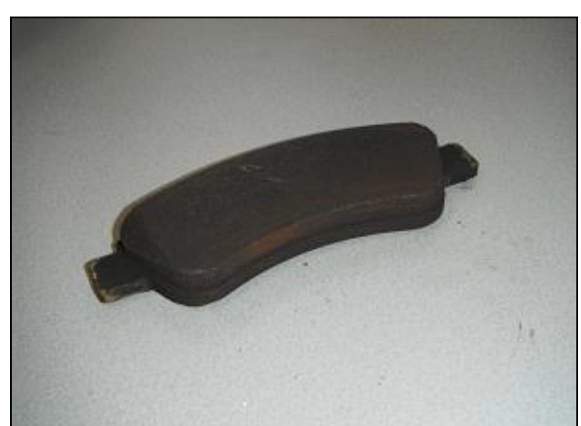

Fig. 1. Example of a collected used brake pad for analysis.