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Ultrafine particle emissions from modern Gasoline and Diesel vehicles: An electron microscopic perspective[☆]

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Ultrafine (<100 nm) particles related to traffic are of high environmental and human health concern, as they are supposed to be more toxic than larger particles. In the present study transmission electron microscopy (TEM) is applied to obtain a concrete picture on the nature, morphology and chemical composition of non-volatile ultrafine particles in the exhaust of state-of-the-art, Euro 6b, Gasoline and Diesel vehicles. The particles were collected directly on TEM grids, at the tailpipe, downstream of the after-treatment system, during the entire duration of typical driving cycles on the chassis dynamometer. Based on TEM imaging coupled with Energy Dispersive X-ray (EDX) analysis, numerous ultrafine particles could be identified, imaged and analyzed chemically. Particles <10 nm were rarely detected. The ultrafine particles can be distinguished into the following types: soot, ash-bearing soot and ash. Ash consists of Ca, P, Mg, Zn, Fe, S, and minor Sn compounds. Most elements originate from lubricating oil additives; Sn and at least part of Fe are products of engine wear; minor W ± Si-bearing nearly spherical particles in Diesel exhaust derive from catalytic coating material. Ultrafine ash particles predominate over ultrafine soot or are nearly equal in amount, in contrast to emissions of larger sizes where soot is by far the prevalent particle type. This is probably due to the low ash amount per volume fraction in the total emissions, which does not favor formation of large ash agglomerates, opposite to soot, which is abundant and thus easily forms agglomerates of sizes larger than those of the ultrafine range. No significant differences of ultrafine particle characteristics were identified among the tested Gasoline and Diesel vehicles and driving cycles. The present TEM study gives information also on the imaging and chemical composition of the solid fraction of the unregulated sub-23 nm size category particles.

1. Introduction

Ultrafine particles (UFPs), i.e. smaller than 100 nm occur in the exhaust of both Diesel, as well as Gasoline vehicles. Soot emission, the principal combustion-generated solid particle pollutant besides metal particles (so-called ash), is of great concern for the environment, as it contributes to global warming and is proven to be hazardous to human health (e.g. Hesterberg et al., 2012; Kennedy, 2007; Künzi et al., 2015; Oberdörster et al., 2004; Steiner et al., 2016; WHO, 2013). Studies on the effects of ash on human health are very limited (Kennedy, 2007) or refer to those found in fly ash (Gilmour et al., 2004; Smith et al., 2000). UFP emissions related to traffic are of special importance, as such small particles deposit with high efficiency in the entire respiratory tract (Oberdörster et al., 2004; Geiser and Kreyling, 2010) and are supposed to be more toxic than larger ones (Bakand et al., 2012; Ruckerl et al., 2011).

Compared to the large bibliography dealing with particulate matter (PM) emissions of Diesel and Gasoline vehicles, relatively few studies are devoted to the ultrafine fraction and the big majority of them are dealing with particle counting research. Issues widely accepted to be currently clarified when counting UFPs and especially their finest fractions are related to the role of the volatile particle removers (VPRs) concerning losses, re-nucleation and supersaturation, as well as the role of all other sampling parts and

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devices from the exhaust up to the Condensation Particle Counter (CPC). It is recalled that with respect to combustion-generated emissions, the so-called 'nucleation mode' comprises mainly volatile organics smaller than ~23 nm and the 'accumulation mode' mainly soot agglomerates and volatile material condensed on the soot agglomerates, which are of larger sizes but mostly in the ultrafine range (e.g. Kittelson, 1998; Kittelson et al., 2006). The presence of PM of the nucleation mode in the vehicle exhaust depends on engine operating conditions and particle measuring techniques (fuel and lubricant used, after-treatment devices, dilution rate, relative humidity, temperature; e.g., Kittelson, 1998; Giechaskiel et al., 2012).

Although numerous studies have been carried out on particle counting, there is an unclear image on the precise nature of the smaller size fraction of the UFPs in the exhaust of Diesel and Gasoline vehicles. It is not always clear whether the smaller sizes of the UFPs are semi-volatiles, volatiles or solid, as there can be artefact particles formed by re-nucleation of (semi)volatiles (Andersson et al., 2007). Based on current particle measurement methodologies, there is a chosen 23 nm cut-off size, as the reproducibility at and below that size has been shown to be poor. The feasibility of lowering the size of measured particles below 23 nm, as a regulatory threshold, was investigated in detail by Giechaskiel et al. (2017). The fraction of the particles below 23 nm could be quantified and characteristic values have been reported for Diesel and Gasoline vehicles, as well as for two and four stroke mopeds. Zheng et al. (2012) and Giechaskiel et al. (2014) have performed extensive investigations in order to exclude possible artefacts associated with the smallest particles. Reviews summarizing the past and current status of the non-volatile particle counting methods and related problems are given by Giechaskiel et al. (2012, 2017).

A powerful tool to investigate the presence and examine the morphology and kind of solid particle emissions in the micro- and nanoscale is electron microscopy, especially transmission electron microscopy (TEM). TEM examines solid particles down to the nanometer scale by applying very high magnification / high resolution (HRTEM). TEM with a sub-nanometer point to point resolution can determine details on the morphology of particles (physically captured on TEM grids) and identify their chemistry by an integrated energy dispersive X-ray system (EDX). (Semi)volatile particles eventually captured on the TEM grids during sampling are clearly distinguished from solid ones either because they evaporate or strongly modify their shape under the high vacuum and/or the influence of the electron beam. It is noteworthy that the strength of TEM analysis relies on high magnification and high resolution, which can reveal important morphological details of particles to extremely low sizes, down to the nanometer scale. Thus, this very high detail cannot go along with solid statistics, as is the case for classically applied particle measuring methods (e.g., SMPS). Thus, statistical inferences based on TEM measurements should be interpreted with care, taking into account the described restrictions.

TEM-studies on ultrafine exhaust particles from Diesel and Gasoline vehicles are limited. Seong et al. (2014) examined nanoparticles from Gasoline direct injection (GDI) engines by TEM. They report a number of UFPs consisting of solid carbon, as well as of young soot (and/or highly condensed semi-volatiles). They also conclude that at low load and retarded fuel injection timing, primary and aggregate particles become extremely small. Saffaripour et al. (2015) investigated by TEM the influence of Particulate Filter and driving cycle (FTP-75 and US06) in GDI engines. They infer that particle emissions in the vehicle equipped with filter over the US06 cycle are ~20% larger. Barone et al. (2012), in a TEM study on the morphology of GDI soot report a prevalence of single solid sub-25 nm particles and fractal-like aggregates under conditions of fuel injection related with low particle number concentrations emissions. Karjalainen et al. (2014) studied exhaust particles from modern (GDI) gasoline vehicles collected over the whole NEDC (New European Driving Cycle). The authors present also some TEM results and report two distinct particle types, namely nearly spherical ones (10 nm to >200 nm) composed of Zn, P, Ca, metals originating from the engine oil, as well as agglomerated soot with ash components (Zn, P, Ca). Studies focusing on electron microscopy of UFPs emitted during the typical driving cycles NEDC and WLTC (Worldwide Harmonized Light Vehicles Test Cycle) employed in tests for the certification of light duty vehicle emissions, are nearly missing.

The present study focusses on TEM analysis of the ultrafine particle size range providing information automatically also on the sub-23 nm size, which is not included in regulations and for which there is a continuously increasing interest in the scientific community dealing with after-treatment research. Within the framework of the present paper, the nature, the particle types, the morphology, the chemical composition and the origin of UFPs in the exhaust of common state-of-the-art on-road vehicle types were studied by TEM. A series of samples were collected at the exhaust of three Gasoline and four Diesel vehicles on the chassis dynamometer. In order to examine whether the exhaust particles are affected by the after-treatment systems of Diesel vehicles, two different exhaust after-treatment settings were employed: (i) one with a diesel oxidation catalyst (DOC) and a Diesel Particulate Filter (DPF), and (ii) one with DOC, DPF and a selective catalytic reduction (SCR) system. During experiments in our Laboratory with the same vehicles, it has been observed that, especially in the cold start phase, the particle number is reduced when a SCR catalyst is added to the DOC + DPF layout, probably due to more available surface for particle deposition. Whether this applies for the ultrafine particle fraction during the entire driving is not known and is included for investigation in this paper.

2. Experimental methodologies

2.1. Setup for PM sampling

PM was collected on TEM grids from three Euro 6b Gasoline vehicles, one operating with GDI and two with port-fuel injection (MPI: multiple point injection) technology, as well as from four Euro 6b Diesel vehicles on a chassis dynamometer. The characteristics of the tested vehicles and driving conditions are summarized in Table 1. Commercially available fuels and lubricating oil from the Swiss market were used.

During the experiments, the exhaust stream downstream of the exhaust after-treatment system (TWC for the Gasoline vehicles and DOC-DPF or DOC-DPF-SCR for the Diesel ones) was guided to the measuring site by a conditioning pipe, as shown in Fig. 1A, heated and diluted by a factor of 13.5. The SCR was working normally during the entire cycle. As the localization of UFPs by electron microscopy on the TEM grids for imaging and chemical analysis is a delicate and complicated task, we tried to optimize the sampling procedure by adding a sampling line which would predominantly collect the smallest particle fraction. Thus, the diluted aerosol was split into two separate flows: one part of the flow was guided to an electrostatic particle sampler (total particle sampler; Fig. 1A) with heated TEM grid sampling and another part to a multi-stage impactor (Electrical Low Pressure Impactor, ELPI; Fig. 1A) with non-installed back-up filter. The particles from the first part passed through a positive loaded corona charger (3.0 kV) and were sampled on a TEM grid fixed on an electrostatic negative loaded holder (- 2.7 kV). The particles from the second part (ELPI) passed a positive loaded corona charger (4.0 kV) and a non-activated ion-