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Metal nanoparticles in diesel exhaust derived by in-cylinder melting of detached engine fragments

Anthi Liati [a, *], Sushant Sunil Pandurangi [b], Konstantinos Boulouchos [b], Daniel Schreiber [a], Yadira Arroyo Rojas Dasilva [c]

[a] EMPA Material Science and Technology, Laboratory of Internal Combustion Engines, CH-8600 Dübendorf, Switzerland
[b] ETH Zürich, Aerothermochemistry and Combustion Systems Laboratory, 8092 Zürich, Switzerland
[c] EMPA, Electron Microscopy Center, CH-8600 Dübendorf, Switzerland

HIGHLIGHTS

- Traffic-related metal nanoparticle emissions can pose environmental and health concerns.
- Fe_3O_4 nanoparticle agglomerates occur in diesel exhaust.
- Steel fragments detached from cylinder engine parts can melt in the combustion chamber.
- A hitherto neglected mechanism of metal nanoparticle formation from internal combustion engines is suggested.

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ABSTRACT

A wide range of environmental and health effects are linked to combustion-generated pollutants related to traffic. Nanoparticles, in particular, are a major concern for humans since they can be inhaled and have potentially toxic effects. The variability and sources of combustion-related nanoparticle pollutants remain inadequately investigated. Here we report the presence of ca. 5–100 nm large Fe_3O_4 nanoparticles, in form of agglomerates, in diesel exhaust. The mode of occurrence of these nanoparticles, in combination with their chemical composition matching that of steel indicate that they derive by melting of engine fragments in the combustion chamber and subsequent crystallization during cooling. To evaluate this hypothesis, we applied CFD simulations of material transport in the cylinder of a diesel engine, assuming detachment of steel fragments from various sites of the cylinder. The CFD results show that fragments $\leq$20 μm in size dislodged from the piston surface or from the fuel nozzle interior can be indeed transported to such hot areas of the combustion chamber where they can melt. The simulation results concur with the experimental observations and point out that metal nanoparticle formation by in-cylinder melting of engine fragments can occur in diesel engines. The present study proposes a hitherto neglected formation mechanism of metal nanoparticle emissions from internal combustion engines raising possible environmental and health concerns, especially in urban areas.

1. Introduction

There is compelling evidence that ambient particulate matter (PM) related to traffic poses environmental and health risks and is associated with an increase in respiratory-related mortality and morbidity (e.g., Barregard et al., 2006; McCreanor et al., 2007; Pope et al., 1995). The role of the metal-bearing fraction of ambient air particles is of particular importance. Transition metals (e.g. Fe, Ni, Cu), in particular, are most likely to have adverse health effects when they are inhaled, i.e. of sub-micrometer size, due to their potential to produce reactive oxygen species in biological tissues (Kelly and Fussell, 2012; Smith et al., 2000). Sub-micrometer large particles have a greater surface area per unit mass, a longer residence time in the atmosphere and can penetrate deeper into the lungs. In addition, metal elements can be adsorbed to atmospheric PM and be deposited to soil, water, and plant leaves via wet and dry deposition.

The exhaust of diesel combustion engines is known to contain a minor fraction of metal-bearing compounds (the so-called ash), apart from abundant carbonaceous components (soot). Ash forms

* Corresponding author.
E-mail address: anthi.liati@empa.ch (A. Liati).

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less than 1% of the total PM emissions (e.g., Sharma et al., 2005) and originates primarily from combustion of low amounts of metals (e.g., Zn, Ca, Mg) added into the lubricating oil to protect engine components. Furthermore, metal fragments (e.g. Fe-, Ni-, Cu-, Cr-, Sb-bearing) abraded mechanically from diverse parts of the engine and/or the exhaust after-treatment systems are also found in the exhaust of diesel engines (e.g., Sappok et al., 2012). Importantly, ash occurs in the exhaust of all types of internal combustion engines, thus increasing its total absolute amount in the atmosphere and therefore its contribution to air pollution and human health effects. The nature, morphology and variability of the metallic fraction of combustion-generated PM remain poorly understood.

During an experimental study dealing with particle emissions in the exhaust of diesel engines at Empa Laboratories, we found by means of transmission electron microscopy, among other metallic phases (Ca–P–Zn–Mg–S-bearing ones related to lube oil and Cr–Ni–Fe-bearing mechanical fragments related to engine wear), branch-like metallic agglomerates of newly formed Fe-oxide nanoparticles. Formation of the above nanoparticles requires very high temperatures that can cause melting of Fe-bearing engine fragment precursors such as steel. Such high temperatures (≥ca. 1800 K; approx. steel melting point) are encountered only in the combustion chamber of the engine.

Within the framework of the present study we (a) describe the detailed electron microscopic characteristics of the Fe-oxide nanoparticles sampled from the diesel exhaust; (b) apply computational fluid dynamic (CFD) simulations to examine whether steel fragments detached from possible sites of the cylinder engine can be indeed transported to areas of the combustion chamber where they can melt, and (c) constrain the possible sources and sizes of the steel fragment precursors that can melt to produce the observed Fe-oxide nanoparticles. For this purpose, we simulated the trajectories of steel particle fragments of different sizes under various scenarios.

2. Experimental

2.1. Sampling

The experiments were carried out on a chassis dynamometer with an Iveco Daily vehicle (MY 2003; Euro IV emission limits) equipped with a 2.3-L 4-cylinder (F1A) common rail diesel engine with turbocharger using commercial fuel (S content <10 ppm) and commercial lubricating oil and fitted with a diesel oxidation catalyst and a diesel particulate filter. For details on the experimental setup the reader is referred to (Liati et al., 2013). Sampling of undiluted exhaust gas was performed under normal operating conditions during steady state operation at 2000 rpm, 13 kW engine speed (70 km/h) and output, respectively using a pump at 0.5 L/min. The temperature of the exhaust gas was approximately 260 °C.

The PM was collected from the exhaust stream directly on 3 mm copper-supported carbon-coated TEM grids by means of an electrostatic particle sampler. The sampling site near the TEM grids was heated to prevent condensation. The sampled material was subsequently analysed by TEM.

2.2. Analytical techniques

For TEM-imaging, a JEOL 2200FS microscope with an Omega filter, a Schottky field emission gun at 200 kV and a point to point resolution of 0.23 nm at the Electron Microscopy Center of EMPA was used. The TEM instrument is equipped with an EDX detector for elemental analysis. TEM analysis was performed using STEM mode (bright field (BF) and dark field (DF)), high resolution (HRTEM) and X-Ray diffraction.

2.3. Simulations – CFD of reacting flow

A CFD simulation was carried out to determine the flow and temperature distribution in time, on the example of a single-cylinder MTU engine at ETH Zürich, for which more details on the overall experimental setup can be found in e.g. (Brueckner, 2014). The commercial CFD solver STAR-CD from CD-adapco Inc. was employed coupled with an in-house code for the turbulent combustion model; the coupling is described schematically in Fig. 1A, while the computational geometry and CFD mesh are shown in Fig. 1B. STAR-CD is a finite-volume based code that computes the Navier–Stokes equations for momentum and energy. The standard PISO solution scheme is employed with the proprietary MARS discretization scheme built into STAR-CD for solving the momentum equations. CHEMKIN is used to obtain chemical reaction rates (ReactionDesign, 2014), which are fed to the CMC code along with pressure and velocity information from STAR-CD, in order to compute the transport and evolution of all chemical species; these in turn are fed back to STAR-CD to continue the iteration cycle. The CMC code adopts a mix of central differencing and TVD schemes for stability. This finite-difference code, detailed in Wright et al. (2005), operates on a coarser CMC-grid synchronized with the CFD mesh. The CFD mesh consists of hexahedral cells with a resolution of 1 mm^3 in the piston bowl resulting in approximately 50,000 cells at top-dead-centre position; at bottom-

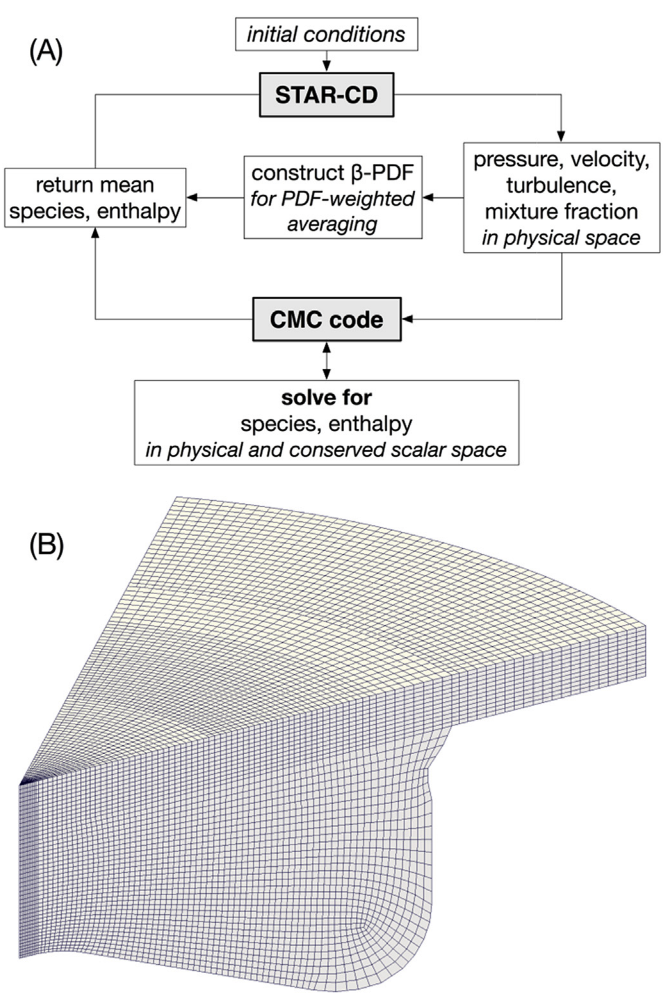

Fig. 1. (A) Schematic illustration of coupling between the flow-field solver (STAR-CD) and the in-house combustion and reacting flow solver based on conditional moment closure; (B) Illustration of the mesh used for numerical simulations.