Characterization and application of a new oxidation flow reactor (DOFR) to study passenger car emissions

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Secondary particle emissions of vehicles are becoming increasingly important aspect for the human health and environment as the primary particle emissions have been efficiently cut down during last two decades by introducing particle filters to vehicles after treatments. Legislation has de facto enforced diesel vehicles to use highly efficient diesel particle filter (DPF) as the particle number emission limits cannot be met otherwise. In addition, gasoline vehicle primary emission limits are becoming stricter in Europe and GDI engines are also increasingly using gasoline filters. Nevertheless, despite more stringent particle emissions norms for tailpipe emissions, the continuous reduction of primary particle emissions has marginally reduced the nucleation mode particle concentrations (e.g., [1]). As a result, the focus is now shifting on the study of secondary emissions, which may have a great impact on health and environment and can be substantially higher compared to primary particle emissions (e.g., [2]).
The oxidation flow reactors (OFR, [3]) are a key tool for investigating secondary aerosol formation processes of different sources. Especially, OFR's are useful tools in studying the photochemical aging of transient emissions sources due their high time resolution compared to environmental chambers and compact size (see e.g., [2], [4]). The high time resolution stems from the short aerosol physical residence time (~1 min) compared to environmental chambers (~hours). Despite of the short physical residence time of the OFRs, the equivalent photochemical aging time can be in the order of several days accomplished by the high concentration of oxidants compared to atmospheric conditions. Despite the fact, that accelerated photochemistry of OFRs have some limitations on how accurately they simulate atmospheric aging [5], OFRs provide properly used a joint metrics that can be used to compare the potential of different emission sources to produce secondary aerosols.

In this study, we present characterization results of a new commercially available OFR called Dekati Oxidation Flow Reactor (DOFR) and its sampling unit. The DOFR design is similar with the previously introduced Tampere University Secondary Aerosol Reactor (TSAR) by Simonen et al. [6]. The main oxidizer in the DOFR is OH-radical that is formed by UV-C (254 nm) photolysis of externally injected O_3 and H_2O. The characterizations performed for the DOFR include the determination of the photochemical ageing range, the residence time distributions (RTD), particle penetration, and the SOA yield of toluene precursor. In addition, the combination of DOFR reactor and the sampling unit were also used for measurement of fresh and aged emissions of several passenger cars (gasoline and diesel) running in idle and the hot and the cold start emissions were compared. Moreover, the setup was used for measuring real-time primary and secondary emissions of passenger cars driven over WLTP driving cycle under different temperature conditions.

Particle size distribution measurements were conducted using the ELPI+ and the SMPS instruments. The particle RTD were measured using two CPCs with polydisperse solid particles. Particle penetration was determined as function of particle size using a CPC and the NanoDMA. The photochemical age was determined with the CO-trace gas method (see, e.g. [6]). Fresh emissions were measured extracting sample from the car tailpipe using cold dilution performed with eDiluter mimicking exhaust dilution to ambient. The fresh emission was then aged with the DOFR setup and secondary aerosol mass measured with ELPI+. Exhaust and toluene precursor ageing inside the DOFR were also modelled with a simple time dependent model based on the model presented by Li et al. [7].

The photochemical age was determined for several relative humidities (RH) and UV-light intensities as a function of O_3 concentration. The ageing range was found to be in 1 – 17 days with the CO tracer and was varied by switching the no. of UV lamps on (the ozone was 50 ppm and RH 50%). The toluene precursor oxidation experiments showed comparable results to previous studies showing 0.1 – 0.3 yields for tested toluene concentrations. The emission measurements showed that tested gasoline vehicles could produce 1 to 4 orders of magnitude more SA mass compared to primary mass with a cold engine. Figure 1. shows the aged PM1 after a cold start and a warm start.

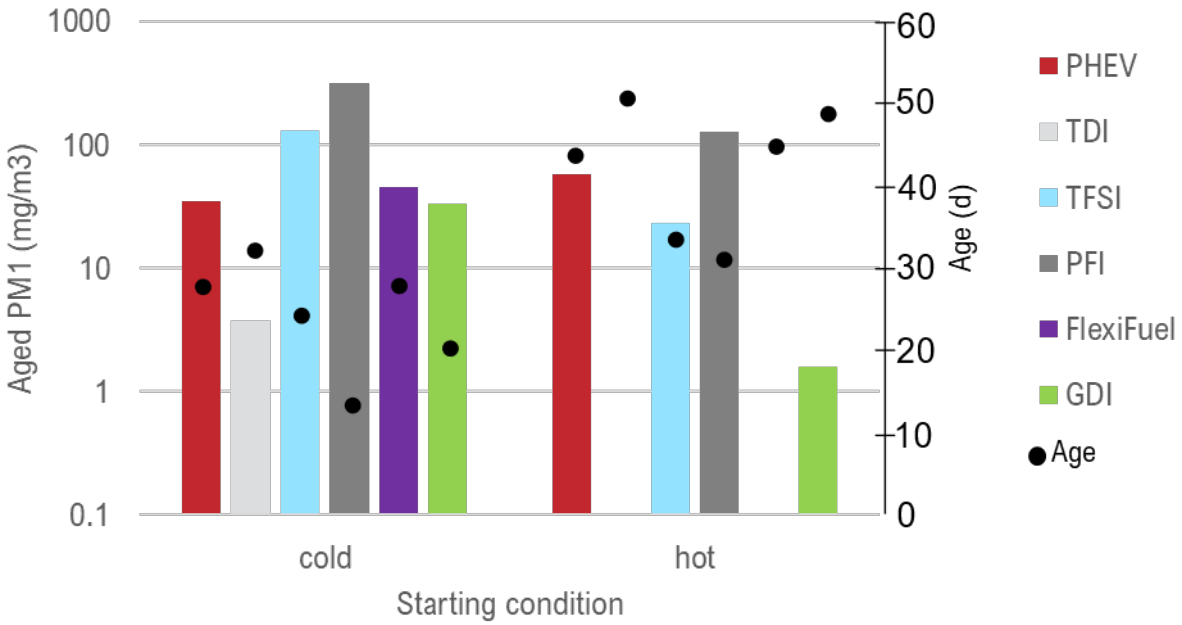

Figure 1. The aged PM1 of idling passenger car exhasut after a cold start and a warm start.

AKNOWLEDGEMENTS

This work was supported by the European Union's Horizon Europe research and innovation programme under grant agreement No 01096133 (PAREMPI: Particle emission prevention and impact: from real-world emissions of traffic to secondary PM of urban air).

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