TNA User Report

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Project title	Determination of the enhancement factor and of the size distribution for secondary PM formed during atmospheric aging of gasoline vehicle exhaust
Name of the accessed chamber	ILMARI
Number of users in the project	2
Project objectives (max 100 words)	Recent studies indicate that secondary particulate matter (PM) originating from vehicular exhaust can be significantly larger than primary PM. The effect of fuel characteristics and engine operating conditions on the formation of secondary aerosol is still not sufficiently investigated and understood. New fuel formulations may have unpredictable impacts on secondary PM formation. The objectives of this project was to develop a procedure to assess characteristics of emissions from gasoline vehicles and for testing the propensity of different gasoline fuels to generate secondary aerosols. Further, the project aimed to characterize the chemical and physical properties of primary and secondary organic aerosols from gasoline vehicles.
Description of work (max 100 words):	A DI-gasoline Euro6b car was used as the emission source and operated by a ROTOTEST chassis dynamometer in different steady engine conditions, using gasoline fuels with different fuel formulations. The emission atmospheric aging processes were simulated in the ILMARI smog chamber by using UV lights (340 nm) and H_2O_2 to generate oxidants. The OH-radical exposures represented approximately four equivalent days of photochemical aging in atmosphere. Particle concentrations, size distribution and chemical compositions as well as VOC concentrations were measured with versatile online instrumentation to determine changes in particle concentrations and physico-chemical properties during aging.

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Trans-National Access (TNA) Scientific Report

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[1] Physics; Chemistry, Earth Sciences & Environment; Engineering & Technology; Mathematics; Information & Communication Technologies; Material Sciences; Energy; Social sciences; Humanities.
[2] UNI= University and Other Higher Education Organisation;
RES= Public Research Organisation (including international research organisations and private research organisations controlled by public authority);
SME= Small and Medium Enterprise;
PRV= Other Industrial and/or Profit Private Organisation;
OTH= Other type of organization.
[3] UND= Undergraduate; PGR= Post graduate; PDOC= Post-doctoral researcher; RES= Researcher EXP= Engineer; ACA= Academic; TEC= Technician.
[4] Reproduce the table for each user who accessed the infrastructure

Instructions

Please limit the report to max 5 pages, you can include tables and figures. Please make sure to address any comments made by the reviewers at the moment of the project evaluation (if applicable, in this case you were informed beforehand). Please do not alter the layout of the document and keep it in Word version. The report will be made available on the eurochamp.org website. Should any information be confidential or not be made public, please inform us accordingly (in this case it will only be accessible by the European Commission, the EUROCHAMP-2020 project partners, and the reviewers). Please include:

- Introduction and motivation
- Scientific objectives
- Reason for choosing the simulation chamber/ calibration facility
- Method and experimental set-up
- Data description
- Preliminary results and conclusions
- Outcome and future studies
- References

Name of the PI: Prof. Andrea D'Anna
Chamber name and location: ILMARI, University of Eastern Finland, Kuopio
Campaign name and period: Determination of the enhancement factor and of the size distribution for secondary PM formed during atmospheric aging of gasoline vehicle exhaust (03.12.2019–17.01.2020)

Introduction and motivation

Modern automotive engines emit very low amounts of pollutants; indeed, the fuel and fuel system, the engine and its combustion system, sensors and the design and location of the catalyst and filter combined with the electronic control system, give nearly maximum emissions reductions. Although the technological progresses, the air quality in dense populated areas characterized by high traffic levels is still very poor. Vehicles contribute to atmospheric PM concentrations not just through their direct (primary) PM emissions, measured at the tailpipe but also through photo-oxidation and gas-to-particle processes of initially gaseous exhaust components (secondary PM). Recent smog chamber studies have shown that secondary particulate matter from combustion engines consists mainly of organic compounds and ammonium nitrate and that the secondary PM formation can be significantly larger than primary PM emissions. The effect of fuel characteristics and engine operating conditions on the formation of secondary aerosol (SA) is still not sufficiently studied and well understood. Emerging fuels and/or new fuel formulations, because of existing differences in conventional fuel composition, may have impacts on SA yield not known or even predictable. Therefore, the effects of strategic formulation or alternative fuels require further studies.
This aspect has induced Eni, an Italian oil company, in collaboration with the Università degli Studi di Napoli Federico II, to study the combustion behaviors and the propensity to form primary particulates and secondary PM precursors of commercial fuels and fuels with new formulations. Moreover, Eni and UNINA would like to develop a measurement protocol, based on smog chamber experiments, to simulate secondary aerosol mass formation potential in order to understand and possible correlate fuel composition with SA formation.

In this context, the activities performed at the ILMARI facility of the University of Eastern Finland aimed at developing a procedure to assess secondary organic aerosol formation potential of different gasoline fuels and to provide information on the formation of secondary PM from the exhausts of modern EURO6 gasoline cars.

Scientific Objectives

The objectives of this TNA-activity were to:
• Develop a representative and reproducible procedure to assess the emission characteristics (both primary and secondary particulate) of automotive fuels and for testing the propensity of different fuels to generate secondary aerosols during their usage in gasoline engines;
• Determine the emission factors of primary and secondary emission components of fuels burning in realistic engines but under controlled lab experiments
• Determine the chemical and physical characterization of primary and secondary organic aerosol as well as their inorganic composition. Regarding aerosol particles, determine the particle size distributions, particle chemical composition and oxidation state of organic aerosol as the function of aging time. Regarding gases, whether SOA formation can be explained by the major known SOA-precursor gases (e.g. benzene, toluene, and xylenes).

Reason for choosing the simulation chamber

This is a multidisciplinary scientific research project needing multiple approach methods (e.g. combustion unit, dilution of emissions, aging, comprehensive physical and chemical analysis) to take full advantage of the research. The ILMARI facility at the UEF has a unique infrastructure which enables us to:

- Operate a passenger car on a dynamometer next to a simulation chamber
- Online monitoring of engine data, driving data, primary gas & particle emissions during driving of the car
- Time-resolved analysis physico-chemical characteristics of particles and gases during aging
- Controlled sampling of exhaust aerosol into the chamber at desired dilution ratio
- Assess all necessary parameters to determine aging conditions (e.g. OH-exposure of during the aging process)

The project also requires special expertise in preparing and running the engine experiments, as well as running the chamber experiments, and specific instruments (gas monitors, particle sizing units, aethalometers).

Method and experimental set-up

As emission source, a DI EURO6b gasoline passenger car was utilized. The vehicle was tested by a ROTOTEST chassis dynamometer in four different engine conditions defined by the velocity and engine load (1-2) or by the engine speed and torque points (3-4):

1. “Cold start and cruising” at 70 km/h (12 kW engine load)
2. “Highway driving” at 120 km/h (38 kW engine load)
3. “High engine power” at 80 km/h, 3000 rpm, 125 Nm
4. “High engine power” at 157 km/h, 5000 rpm, 93 Nm

Two gasoline fuels were used in the experiments: E10 and E5 having different alcohol contents. A partial flow of exhaust was sampled using a porous tube – ejector diluting sampling setup and injected into the transformation chamber. The sample dilution ratio was controlled by using CO2 as marker gas. The gaseous primary emissions were measured continuously by using a FTIR-multicomponent gas analyzer (Gasmet DX4000, e.g. CO2, CO, NOx, 30 organic gas compounds), single NDIR-based gas analyzers for NO, CO and CO2 (Siemens) and a flame ionization detector (FID, Siemens) for total organic gases. The primary particles were measured online using a Fast Mobility Particle Sizer (FMPS, TSI) and two different Scanning Mobility Particles Sizer systems (SMPS, TSI) ; one measuring particles down to 3 nm and the second one measuring a broader size distribution between 15 nm and 661 nm.

The transformation process of vehicular exhaust was simulated using the ILMARI chamber. It is a 29 m3, air-conditioned FEP Teflon chamber with UV blacklights (centered at 340 nm), humidification systems and ozone generators. After feeding the sample into the chamber, it was mixed and stabilized for roughly 20 minutes to determine the primary aerosol characteristics. After stabilization and mixing in the chamber, additional oxidants (for most experiments only H_2O_2) were injected into the chamber. The UV lights were switched on and the aerosol was aged under UV light for 4 h representing up to four day of atmospheric ageing. Chemical and physical properties of the aerosol particles and gases during the aging process were measured using on-line measurements of aerosol concentration and size distribution (SMPS), black carbon (Aethalometer, Magee Scientific), fine particle chemical composition (SP-AMS-ToF) and VOC and semi-VOC (HR-PTR-ToF). In addition, NO, NO_2, O_3, RH, and temperatures were measured continuously from the chamber (Figure 1).

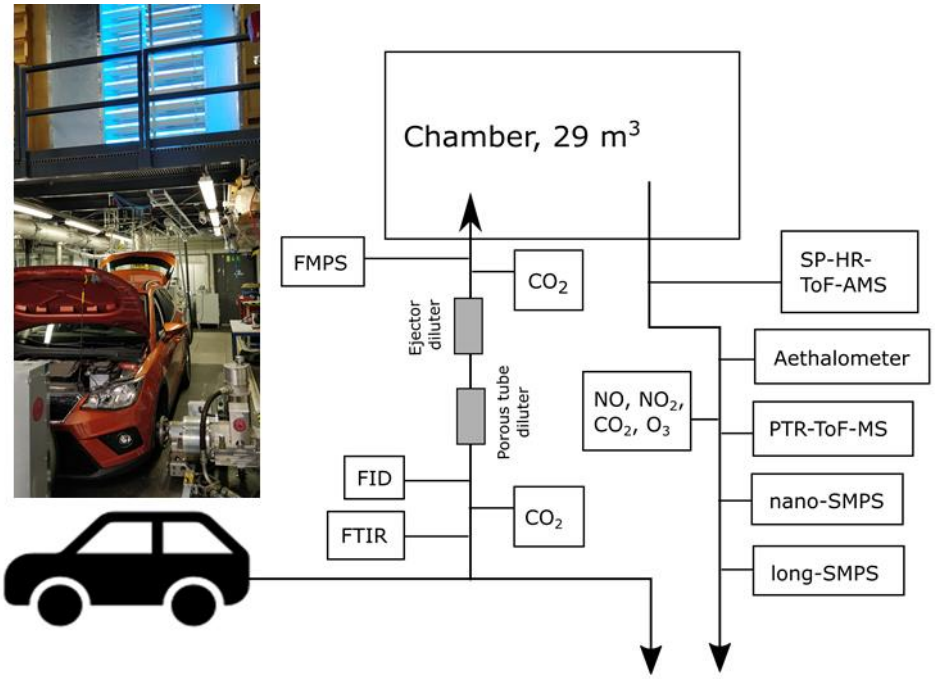

Figure 1. Experimental setup

Data description

The experiments provided versatile and unique data on gasoline engine emissions and their aging. In particular the data will be used to determine:

- Emissions of aromatic VOC and their decomposition during aging
- Emissions and secondary formation of oxygenated VOCs
- Primary organic (POA), Secondary organic (SOA) and inorganic (SIA) aerosol emissions and the related aerosol enhancement factors as the function of photochemical OH-exposure
- Particle size distributions as the function of photochemical age
- Effects of driving conditions on primary emissions and on the secondary aerosol formation
- Effects of fuel formulation on primary emissions and on the secondary aerosol formation

Preliminary results and conclusions

Exhaust concentrations of primary gaseous emission that influence secondary aerosol formation measured at the exhausts of the vehicle burning standard E5-gasoline and higher-alcohol content gasoline E10 are reported in Figure 2. The highest concentrations of non-methane volatile organic compounds (NMVOC) were measured in the "high engine power" experiments. In addition, the cold start generated substantial NMVOC concentrations. Interestingly, for E10 fuel, clearly lower NMVOC concentrations were measured in the "high engine power" driving setting. The driving setting and fuel affected also NOx and NH_3 emission levels (Figure 2). Both "high engine power" and "cold start & cruising" settings generated notable NH3 and NOx emissions, whereas during the "highspeed driving" these emission components remained at low levels. In gasoline cars, NH3 is formed in the three-way catalyst under rich conditions (Suarez-Bertoa et al., 2019). The conversion of the primary emission results to emission factors, to relate the emission concentrations to the travelled distance, will be carried out as soon as all the necessary data has been processed.

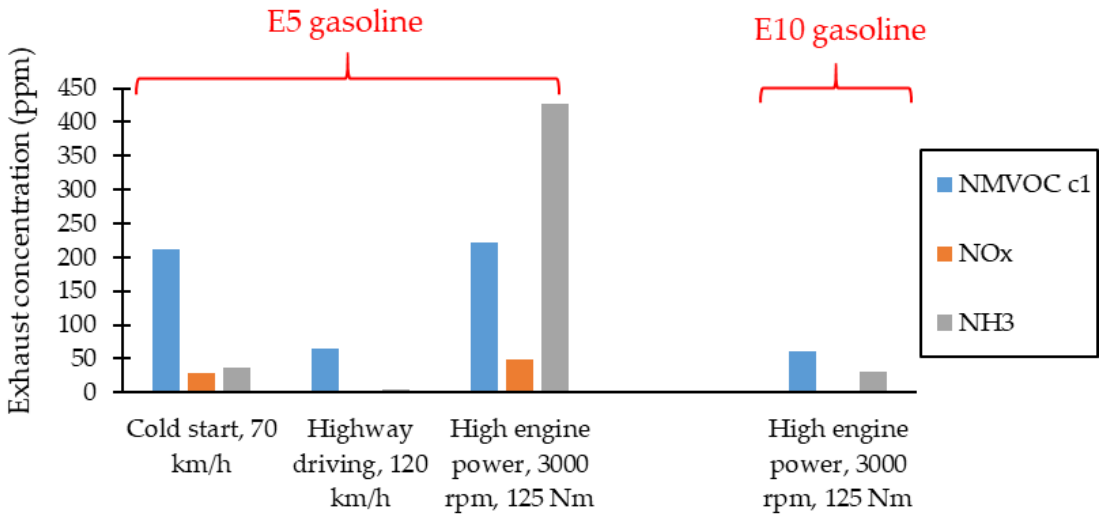

Figure 2: Exhaust concentrations of primary gaseous emission that influence secondary aerosol formation: Comparison of standard E5-gasoline and higher-alcohol content E10 gasoline.

The particle size distributions in the fresh exhaust were dominated by nanoparticles below the diameter of 100 nm (Figure 3). The highest particle number concentrations were emitted in the high engine power (5000 rpm) conditions, whereas cold start & cruising generated on average largest particles with the lowest number concentrations.

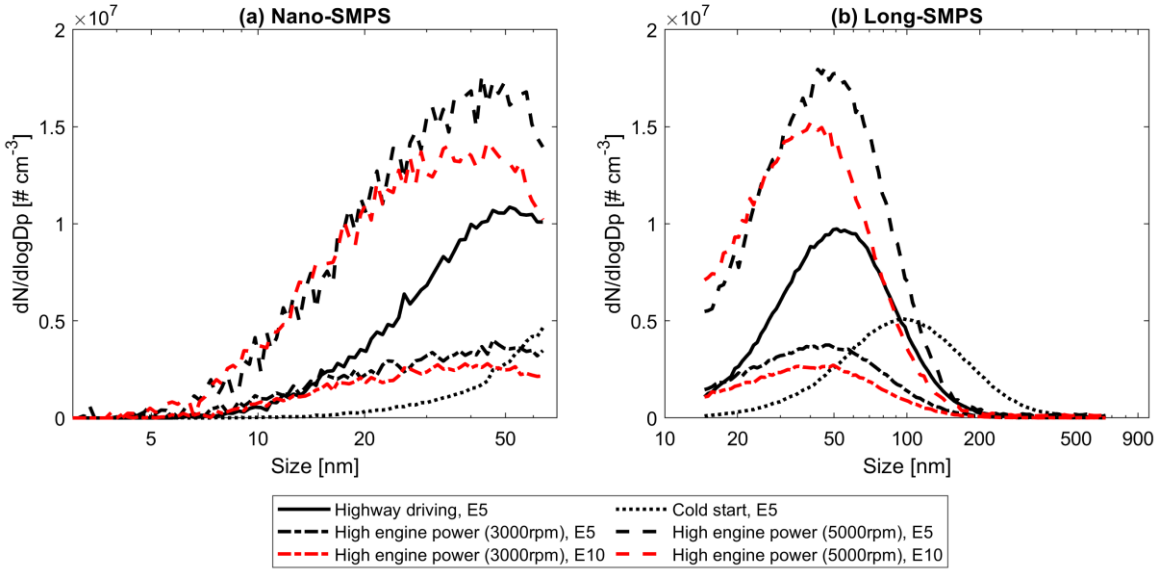

Figure 3: Dilution corrected particle size distributions in primary emissions with different fuels and driving conditions measured from the chamber during stabilization period by two scanning mobility particle sizer (SMPS) systems: (a) a "nano-SMPS" capable of measuring down to 3 nm in particle size and (b) a "Long-SMPS" measuring from 15 nm to 661 nm in particle size.

The preliminary results on the wall-loss corrected concentrations of particulate organic matter, as measured by the SP-AMS-ToF, during the chamber experiments are depicted in Figures 4 and 5. In each chamber experiment, a clear increase in particulate organic aerosol concentration was observed, as a result of secondary organic aerosol formation. The repeated chamber experiments with same driving condition/fuel had a good reproducibility in terms of primary organic aerosol (POA) concentrations and the organic aerosol enhancement during the UV-light induced aging process (Figure 4).

Overall, the emission factors of organic emissions and the organic aerosol enhancement ratios were largely dependent on the driving conditions. The preliminary results on POA emissions determined with the SP-AMS for the E5 gasoline are 92 µg/km, 77 µg/km and 122 µg/km for the "cold start & cruising", "highway driving" and "high engine power" cases, respectively. The OA enhancement during aging varied by a factor of 3 to 65 with the highest enhancement factors in the "cold start & cruising" and "high engine power" cases. SOA formation in case of the higher alcohol containing gasoline (E10) was lower than for E5 gasoline in the high engine power 3000 rpm setting, but comparable in the high engine power 5000 rpm case.

The different NOx and NH_3 emission levels (Figure 2) of different experimental cases influence the emission transformation process in multiple ways. Firstly, significant secondary nitrate aerosol formation was observed in the chamber in the experiments with both high NOx and ammonia levels. Second, the VOC:NOx -ratios varied in the experiments, ranging from 5 to > 100, which may affect the SOA yields of the precursors. The SOA yields and specific SOA-precursors will be investigated after the complete analysis of mass spectrometer data is available.

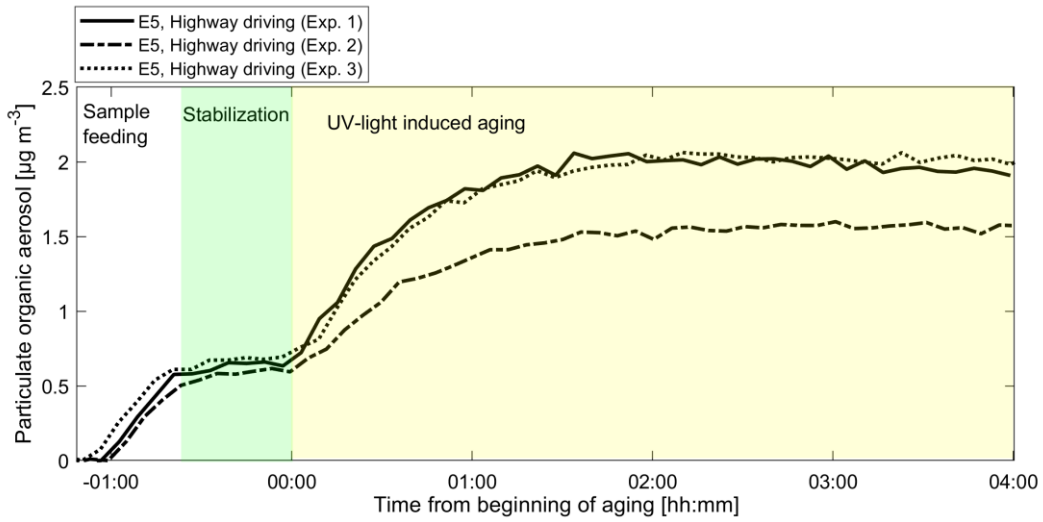

Figure 4: Wall-loss-corrected organic aerosol time series during the aging experiments with the E5 standard gasoline and "highway driving" condition. The repetitions indicate good repeatability for the experiments in terms of organic aerosol emissions concentrations and their time-dependent behavior in the chamber.

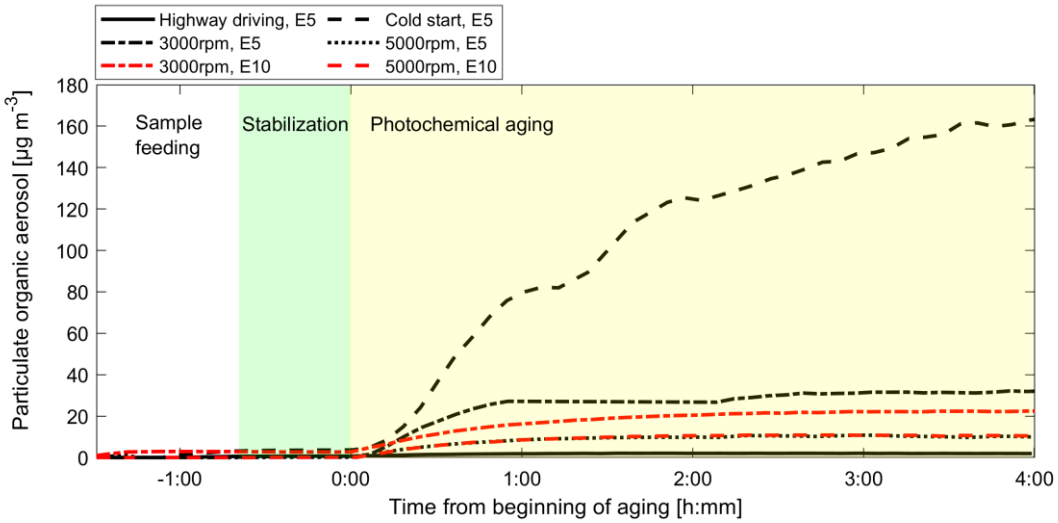

Figure 5: Wall-loss-corrected organic aerosol time series during the aging experiments with different fuels and driving conditions.

Outcome and future studies

Transformation of gasoline car emissions during photochemical aging was investigated using different driving conditions with high emission levels (e.g. cold start and high torque engine points). The used experimental procedure for assessing the formation of secondary aerosols was found to have a relatively good repeatability. The experiments were successful and the preliminary results indicate clear differences in the exhaust SOA-formation potential of different fuels. The results contain also valuable information on the SOA formation potential of gasoline exhaust from vehicles equipped with the latest exhaust after-treatment technologies. More detailed analysis of the results will be carried

out soon to investigate the propensity of different fuel formulations to form SOA pollution and to acquire more detailed analysis on how photochemical aging changes the physico-chemical characteristics of the exhaust aerosol particles.

References

Suarez-Bertoa, R., Lähde, T., Pavlovic, J., Valverde, V., Clairotte, M., Giechaskiel, B. (2019) Laboratory and on-road evaluation of a gpf-equipped gasoline vehicle. Catalysts 9, 678; doi:10.3390/catal9080678