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# Multi-technique physico-chemical characterization of particles generated by a gasoline engine: towards measuring tailpipe emissions below 23 nm

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## Abstract

Particulate emissions from on-road motor vehicles are the focus of intensive current research due to the impact of the ambient particulate matter (PM) levels on climate and human health. Constant improvement in engine technology has led to significant decrease in the number and mass of emitted PM, but particular concern is raised nowadays by the ultrafine particles. In this context, there is a critical lack of certification procedures for the measurement of the smallest-size (<23 nm) particulate matter emissions. To support the engine development process as well as future certification procedures, a measurement technology for sub-23 nm particles must be designed. The development of a reliable measurement procedure entails understanding the formation and evolution of particles from the engine to the tailpipe via multiple analytical techniques and theoretical simulations.

We present here extensive experimental characterization of ultrafine particles emitted by a gasoline direct injection single-cylinder engine as particle generator. The particles were sampled using a cascade impactor which allows size-separation into 13 different size bins. Chemical characterization of the collected size-selected particles was performed using mass spectrometry, which gives access to detailed molecular information on chemical classes of critical interest such as organosulphates, oxygenated hydrocarbons, nitrogenated hydrocarbons, metals, or polycyclic aromatic hydrocarbons. Additionally, the morphology of the emitted particles was probed with atomic force (AFM) and scanning electron microscopy (SEM). Tip-Enhanced Raman Spectroscopy (TERS) was applied for the first time to sub-10nm combustion-generated particles to gather information on their nanostructure. The extensive database built from these multiple experimental characterizations has been used as input of a theoretical approach to simulate and validate engine out-emissions. These studies were performed in the framework of the H2020 PEMS4Nano project which aims to the development of a robust, reliable and reproducible measurement technology for particles down to 10 nm for both chassis dyno and real driving emissions (RDE).

**Keywords:** Internal combustion engine, nanoparticles, physico-chemical characterization, mass spectrometry, emission modeling

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## 1. Introduction

The particulate matter (PM) is a ubiquitous air pollutant, consisting of a mixture of solid and liquid particles that can remain suspended in the air, ranging from a few minutes up to days or even weeks depending on their size, and hence undergo long-range transport (World Health Organization, 2013). Primary PM can have anthropogenic sources which include PM produced by internal combustion (IC) engines (*e.g.* on-road vehicles), wear of vehicle components, or industrial activities. Traffic is therefore a significant source of PM emission having a mass size distribution ranging from coarse mode ( $PM_{10} < 10 \mu m$ ) to fine mode ( $PM_{2.5} < 2.5 \mu m$ ) particles (Atkinson et al., 2010), and often dominated by submicron particles (*e.g.*  $PM_{0.5} < 0.5 \mu m$ ). Major improvements in engine technology and the use of alternative fuels over the last few years have helped contain the environmental harm caused by PM emissions (Raza et al., 2018). While  $NO_x$  and hydrocarbons emissions have been reduced along with the mass and number of emitted particles, one of the downsides has been the shift in the particle diameter towards smaller sizes (lower than 100 nm (Karjalainen et al., 2014)), thus likely contributing to air pollution, *i.e.* a public health issue (*e.g.* Manke et al. (2013); Sager and Castranova (2009); Seaton et al. (2009); EPA (2009)). The G-20 countries account for 90% of global vehicle sales, and 17 out of the 20 members have chosen to follow the European regulatory pathway for vehicle emissions control (Williams and Minjares, 2016). Therefore, information about the particle number (PN) of ultrafine particles is becoming more and more valuable for vehicle certification. Specifically, sub-23 nm particles have recently attracted a lot of attention for mainly two reasons. For one, sub-23 nm particles can be produced, and sometimes in high concentrations, in both diesel and gasoline direct injection (GDI) engines (*e.g.* Giechaskiel et al. (2014)). Second, the harmfulness of the particles has been shown to correlate better with surface area than with mass (Donaldson et al., 1998; Oberdorster, 1996), which becomes important for ultrafine particles even though their residence time in the atmosphere is shorter. However, it has been estimated that the percentage of sub-23 nm solid particles that is not measured by current certification procedures (that have a cut-off size of 23 nm) could reach 30-40% of the total PN for gasoline vehicles utilizing direct injection, and be potentially higher when alternative fuels are being used (Giechaskiel et al., 2017). Therefore, the critical lack of certification procedures for the measurement of ultrafine ( $< 23$  nm) particulate matter emissions should be addressed. Current efforts (Kontses et al., 2020; Chasapidis et al., 2019; Lee et al., 2019) focus on providing solid scientific ground to allow lowering the 23 nm limit to 10 nm, with the aims of providing robust particle number measurement methodology and associated instrumentation. Although possible in principle (at least in well-controlled laboratory conditions), going below this limit appears as very challenging as nanometer-size particles raise important sampling, measurement and quantification issues which can result in undesired biases and artifacts (Simonen et al., 2019). This difficulty is of course enhanced when designing reliable portable measurement systems dedicated to monitoring nanoparticle emissions in real-driving conditions.

The development of a robust and reliable certification procedure for measuring even small particles requires a good understanding of the characteristics of the emitted particles. There are several studies that examine particle emissions of modern direct injection engines during laboratory tests (chassis dynamometer) and even under real driving conditions. The number, mass, and size distribution of emitted particles have been already studied for a wide variety of engine operating conditions (Khalek et al., 2010; Baral et al., 2011; Maricq et al., 2011; Karjalainen et al., 2014; Vojtíšek et al., 2014; Momenimovahed et al., 2015; Ko et al., 2019). It was also shown that engine emissions tend to be optimized for the certification test cycle, while other regimes are often overlooked (Vojtisek-Lom et al., 2009; Weiss et al., 2011). As a result, engine emissions in real driving conditions (RDE) tend to be higher (Kayes et al., 2000; Kristensson et al., 2004). The chemical composition of exhaust particles was also examined and enabled the estimation of fuel and oil contribution to elemental (EC) and organic carbon (OC) (Kleeman et al., 2008; Fushimi et al., 2016; An et al., 2016). However, there is still very little information about the chemical composition of fine and ultrafine particles emitted by modern engines and their origin. The latter is especially important for the development of a Particle Measurement Program (PMP) capable of measuring ultrafine particles, below 23 nm (Zheng et al., 2011).

To explore the physico-chemical characteristics of the emitted particles, it is necessary to perform a multi-technique analysis of GDI engine emissions. The objective of this study is to build a large database through a

thorough size-dependent physico-chemical characterization of a wide variety of combustion-generated particles sampled under different engine operating conditions. The database includes extensive information about the size-dependent molecular-level chemical composition of emitted particles as small as 10 nm obtained with high-performance mass spectrometry techniques. Recently developed advanced statistical methodologies (Irimia et al., 2018, 2019; Duca et al., 2019), based on principal component analysis (PCA) and hierarchical clustering analysis (HCA), are used in this work to highlight subtle differences, as well as similarities, between different-sized particles. These data are complemented by the particle morphology information obtained with a scanning electron microscope (SEM) and an atomic force microscope (AFM), while unprecedented tip-enhanced Raman spectroscopy (TERS) measurements on individual combustion-generated particles down to a few nm are performed to gather insights about their nanostructure. Engine set-points used for off-line characterization of particles were selected using laser induced incandescence (LII) – an on-line measurement technique able to provide real-time information on the PM size-distribution and volume fraction. The obtained database is then utilized in a theoretical approach (referred to as Model Guided Application – MGA) which combines detailed physico-chemical simulation together with advanced statistical techniques of parameter estimation, computational surrogate generation and sensitivity analysis (Lee et al., 2019). The MGA aims to predict the particle formation in the engine, as well as particle dynamics in the exhaust system and sampling line. Although the modeling work presented in this paper is related to a single-cylinder test engine (used as a particle generator), the knowledge gained here (experimental and theoretical) can be easily transferred to multi-cylinder engines and even expanded to drive cycle simulations, thus providing crucial information for the development and optimization of particle emission monitoring systems (PEMS). These studies were carried out in the framework of the H2020 PEMS4Nano project ([www.pems4nano.eu](http://www.pems4nano.eu)) where a bottom-up approach was adopted in order to develop a robust, reliable and reproducible particle emission monitoring system (PEMS) for both chassis dyno and real-driving conditions.

## 2. Materials and Methods

### 2.1. Single cylinder engine and sampling line

The particulate matter investigated in this work was produced by a generic gasoline direct injection single-cylinder test engine, whose specifications are given in Table 1. The engine was operating on Euro Stage V E5 Gasoline (CEC-RF-02-08 E5). The temperature for both coolant and oil (Agip SIGMA, 10W-40) was set to 80°C. All the operating points studied are described in Table 2 (*e.g.* applied load, injection timing). For all the set-points, the engine was operating at 2000RPM with the ignition timing set for the maximum brake torque (MBT). Between each operating point, the engine was operated with methane (CH<sub>4</sub>) for 30 minutes to ensure the cleanliness of the combustion chamber.

Table 1: Engine specifications (b/aTDC – before/after Top Dead Center)

Specification	Value
Cylinder head	Pentroof type
Compression ratio	12.5:1
Bore	82 mm
Stroke	85 mm
Stroke volume	449 cm <sup>3</sup>
Fuel direct injection system	Central mounted generic six-hole injector
Injection pressure	150 bars
Spark plug location	Exhaust side
Intake valve timing:	Open 334 deg. bTDC
	Close 166 deg. bTDC
Exhaust valve timing:	Open 154 deg. aTDC
	Close 330 deg. aTDC

Monitoring and sampling of particles from the generic single-cylinder test engine was performed using a home-built sampling line. A partial flow was taken from the exhaust duct approximately 5 cm after

86 the exhaust port and was then supplied via 8 cm long transfer line to DEKATI FPS 4000 (Fine Particle  
 87 Sampler) two-stage dilution system (1:3 and 1:10 dilution ratios for the hot (180°C) and cold (35°C)  
 88 stages respectively). The rest of the exhaust flows through an optical cell for on-line soot monitoring by LII.  
 89 As detailed below, the LII technique was used for preliminary characterization and selection of the engine  
 90 operating conditions. Additionally, the in-cylinder pressure profile and gas phase emissions (CO,  $\mu$ HC and  
 91  $\text{NO}_x$ ) were monitored.

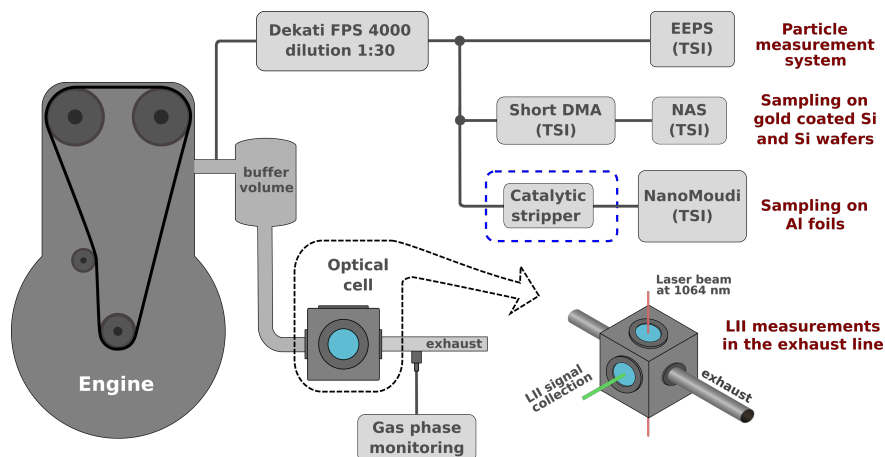


Figure 1: Schematic representation of the sampling line. Sampling with NanoMoudi on Al foils can be done with or without the catalytic stripper (dashed blue rectangle).

92 After dilution, the flow of particles was split into three branches. On the first one, an Engine Exhaust  
 93 Particle Sizer (EEPS; TSI, model 3090) was used to measure particle number and size distribution. A  
 94 combination of a Nano-Differential Mobility Sizer (Nano-DMA; TSI, model 3085) and a Nanometer Aerosol  
 95 Sampler (NAS; TSI, model 3089, Fig. 1), placed on the second branch, was used to collect particles for  
 96 structural and morphological analyses, thus enabling sampling within very narrow size bins. Finally, the  
 97 sampling for chemical analysis was conducted on the third branch with a NanoMOUDI II cascade impactor  
 98 (TSI/MSP, model 125R). Being a “Micro-Orifice Uniform-Deposit Impactor”, the NanoMoudi works on the  
 99 well-known principle of inertial impaction (Marple et al., 1991; Marple, 2004). The MOUDI impactors have  
 100 sharp stage characteristics with steep cut-offs and low inter-stage wall losses. The used model comprises 13  
 101 stages, with nominal cut-off sizes of 10000, 5600, 3200, 1800, 1000, 560, 320, 180, 100, 56, 32, 18, and 10  
 102 nm. Particles were deposited on uncoated aluminum foils (heated for 12 hours in an oven at 300°C prior to  
 103 the sampling).

104 A catalytic stripper (CS) can be placed before the NanoMoudi in order to investigate its impact on  
 105 the properties of the particles sampled in several engine regimes. The CS was built by the University of  
 106 Cambridge in a similar fashion to the commercially-available models (Catalytic Instruments). The coating  
 107 was commercially available precious metal loading (100–300 g/m<sup>2</sup>) with an alumina wash coat. The CS was  
 108 calibrated and monitored with a temperature controller to ensure that the centerline temperature of the  
 109 aerosol achieves 350°C prior to entering the catalytic monolith contained within the device. The catalytic  
 110 stripper performance in terms of hydrocarbon removal was tested to be >99% for 30 nm tetracontane  
 111 particles at a concentration of >10<sup>4</sup> cm<sup>-3</sup>. The precise catalyst chemistry has not been measured. The  
 112 penetration efficiency was >60% for 10 nm particles and the entire system residence time was 1–2 s. The  
 113 influence of the catalytic stripper on particle characteristics was studied since its usage in a PMP compliant  
 114 system and is preferred over an evaporative tube (ET) as it significantly reduces the number of artifact  
 115 ultrafine particles formed by renucleation of semivolatiles, thus considerably increasing the reliability of the  
 116 system (Zheng et al., 2011). The stripper was operating at 370°C and was preheated prior to the sampling.

117 The off-line characterization techniques used for structural and morphological analysis (described in  
 118 section 2.3.1) require samples with a low coverage, *i.e.* isolated individual particles. At the same time, the  
 119 chemical characterization (Section 3.3) requires more loaded samples, ideally with a homogeneous layer of

120 particles fully covering the deposition substrate. Consequently, the sampling time for the samples intended  
 121 for chemical characterization was much longer. Moreover, to obtain similar coverages, the time was optimized  
 122 for each engine operation regime, the longest (12h) being for the **NHC** regime and the shortest (6h) for  
 123 the **EM** one, respectively (Table 2). Regarding the samples intended for the structural and morphological  
 124 analysis, the collection time varies between 30 minutes and 1h, depending on engine conditions.

Table 2: Studied engine operating points (IMEP – Indicated Mean Effective Pressure,  $\lambda$  – ratio of the actual air/fuel ratio to stoichiometric). “Optimal engine conditions” refer to optimal injection and ignition timings set for MBT.

Set-point	IMEP, bar	$\lambda$ $\pm 0.01$	Injection deg. BTDC	Comments
NS	3	1.01	270	
NM	6	1.01	270	
NH	12	1.01	270	
NHC	12	1.01	270	With a catalytic stripper
OM	6	1.01	270	Addition of oil
EM	6	0.70	270	Low air/fuel ratio
EI1	12	1.01	305	Early injection
EI2	12	1.01	311	Early injection

“N” in the set-point designations stands for normal engine operation (optimal engine conditions); “S/M/H” – small/medium/high load applied to the engine; “C” – catalytic stripper; “OM”, “EM” – malfunction regimes (“O” – addition oil; “E” – excess of fuel resulting in low air/fuel ratio); “EI” – optimal air/fuel ration, high load, early injection.

## 125 2.2. On-line characterization by Laser-Induced Incandescence

126 LII is a laser-based technique allowing soot concentration monitoring in various environments, for instance  
 127 in flames (Schulz et al., 2006) and in the combustion chamber of internal combustion engines (Boiarciuc  
 128 et al., 2007; de Francqueville et al., 2010; Koegl et al., 2018). LII also proved to be suitable to control  
 129 real time soot emission directly in the exhausts of diesel (Case and Hofeldt, 1996; Bachalo et al., 2002),  
 130 gasoline (Smallwood et al., 2001; Bardi et al., 2019), and aeronautical engines (Delhay et al., 2009). In  
 131 this work, the objective of the LII measurements is to study the evolution of the soot volume fraction with  
 132 engine conditions in order to select the appropriate engine set-points for off-line soot-characterization. The  
 133 principle of LII consists first in heating combustion-generated particles up to 3500-4200K, generally using a  
 134 pulsed laser, and then recording the radiation associated with the thermal emission while they cool down.  
 135 This incandescence emission follows the Planck law and depends on the emission properties of particles at  
 136 the detection wavelength. LII is mainly used to determine the soot volume fraction ( $f_\nu$ ) and the primary  
 137 particle diameter (Schulz et al., 2006). Soot volume fraction can be determined from the time-resolved LII  
 138 peak signal as follows:

$$f_\nu \propto \left( \frac{LII}{E(m_\lambda) \cdot B(T, \lambda)} \right) \quad (1)$$

139 where  $B(T, \lambda)$  is the Planck function,  $T$  is the peak reached temperature,  $\lambda$  - the emission wavelength,  $m_\lambda$   
 140 - the refractive index of the particle and  $E(m_\lambda)$  - soot absorption function.

141 The decay of the LII signal is related to the cooling time of particles and therefore to their size. Primary  
 142 particle diameter can hence be determined, provided a model of the energy transfer during laser heating  
 143 is available (Michelsen et al., 2007; Betrancourt et al., 2017). The LII technique has been continuously  
 144 developed and optimized at University of Lille during the last decades (Bladh et al., 2006; Bejaoui et al.,  
 145 2014). It has been applied to, e.g., the measurement of the soot volume fraction in turbulent flames  
 146 (Lemaire et al., 2010) or in the exhaust of aero-engines (Delhay et al., 2009). Recent efforts were devoted  
 147 to the detection of very small soot nanoparticles (Betrancourt et al., 2017, 2019). The LII technique was  
 148 adapted here to probe soot particles in an optical cell mounted on the exhaust duct (Fig. 1), simultaneously

149 with PM collection for off-line analyses. The choice of the optimum cell location took into consideration  
150 the layout and space constraints of the test bed. Details of the LII experimental set-up are provided in the  
151 Supplementary Fig. S1. Briefly, LII measurements were performed with an excitation wavelength of 1064  
152 nm generated by a Nd:YAG pulsed laser (Quantel Brilliant, 10 Hz repetition rate, 5 ns pulse duration). An  
153 optical attenuator is used to adjust the energy of the laser between 0 and 350 mJ/pulse. The excitation  
154 laser beam has a Gaussian profile and a diameter of 6 mm. A laser fluence of 0.32 J/cm<sup>2</sup> was used for  
155 excitation, thus maximizing the LII signal and limiting its dependence on laser fluctuations. The LII signal  
156 is collected by two achromatic lenses ( $f_1=200$  mm,  $f_2=100$  mm) and focused on the collection slit (100 mm x  
157 0.2 mm). The signal, in the 400-825 nm spectral range, is then detected with a photomultiplier tube (PMT)  
158 (Hamamatsu R2257) and recorded by an oscilloscope (LeCroy 6050A, 500 MHz bandwidth, 5 GS/s sampling  
159 rate) triggered with a photodiode (Hamamatsu S1722-02). The PMT is equipped with a short-pass filter  
160 with a cut off at 825 nm. The performance of the set-up (with exactly the same geometry and collection  
161 volume) was priorly optimized and evaluated in the laboratory of Lille using carbon particles produced  
162 by a PALAS DNP 2000 generator. Set-points providing nearly constant particles concentrations could be  
163 obtained in the range  $10^5$  to  $1.2 \cdot 10^6$  particles/cm<sup>3</sup>. From these measurements a limit of detection of  $10^4$   
164 particles/cm<sup>3</sup> was established.

### 165 2.3. Off-line characterization

#### 166 2.3.1. Morphology and structure

167 For structural and morphological studies, particles collected on Au-coated or bare Si wafers are analyzed  
168 with Scanning Electron Microscopy (SEM) and Atomic Force Microscopy / Tip Enhanced Raman Spec-  
169 trometry (AFM/TERS). The SEM Merlin (Zeiss) is used for the morphology analysis of collected particles;  
170 it features a spatial resolution of 1 nm and high detection efficiency. For the study of ultra-fine particles, a  
171 low accelerating voltage (1kV) was chosen to decrease the size of the interaction volume and improve the  
172 spatial resolution. Moreover, it enables the study of ultra-fine combustion-generated particles without the  
173 need of a conductive coating. Additionally, SEM images are used to determine the surface coverage and  
174 adjust, if needed, the sampling time.

175 The AFM (SMART SPM, HORIBA Scientific) features high-resolution cantilever-based tips (Hi'Res-  
176 C14/Cr-Au,  $\mu$ masch, typical 1 nm-radius) for a high lateral resolution. A NanoRaman system that combines  
177 a SMART-SPM (HORIBA Scientific) with a Raman spectrometer (LabRAM HR Evolution Nano, HORIBA  
178 Scientific) is used for tip-enhanced Raman measurements (TERS). The system is based on a reflection  
179 configuration allowing the use of a 100x objective lens (NA 0.7) with a 60° angle. The incident laser  
180 (633 nm, p-polarized) is focused through the objective onto the apex of the cantilever-based silver TERS  
181 probe (Ag coated OMNI TERS probe). The collection of the back-scattered signal is performed through the  
182 same objective. The reliable stability of the whole system allows to maintain the laser-tip alignment and  
183 accurate XYZ position during the TERS map acquisition (at least 1 hour).

#### 184 2.3.2. Chemical composition

##### 185 Two-step laser mass spectrometry

186 Our group has extensively developed the two-step laser mass spectrometry (L2MS) technique over the last  
187 decade to specifically probe the chemical composition of combustion byproducts (Popovicheva et al., 2017;  
188 Delhaye et al., 2017; Faccinnetto et al., 2011, 2015; Moldanová et al., 2009). The main advantages of L2MS  
189 are its high sensitivity and selectivity with regards to specific classes of compounds owing to the resonant  
190 ionization processes that can be adapted, by using different ionization wavelengths, thus targeting different  
191 classes of compounds and reaching sub-fmol limit of detection, *e.g.* for PAHs (Faccinnetto et al., 2008, 2015).  
192 Systematic studies (Mihešan et al., 2006, 2008) have led to the optimization of the laser desorption process  
193 (and its coupling with the subsequent ionization step (Faccinnetto et al., 2008), which ensures a soft removal  
194 (with minimum internal excess energy) of molecules adsorbed on the particle surface, and thus avoids/limits  
195 both their fragmentation and the in-depth damaging of the underlying carbon matrix (Faccinnetto et al.,  
196 2015). In this work, a new mass spectrometer (Fasmatech S&T) is used, combining ion cooling, Radio  
197 Frequency (RF) guiding and Time of Flight (ToF) analyzer, which allows us to reach a mass resolution of

198  $m/\Delta m \sim 15\,000$ . In this new experimental setup, the sample, placed under vacuum ( $10^{-8}$  mbar residual  
 199 pressure), is irradiated at  $30^\circ$  angle of incidence by a frequency doubled Nd:YAG laser beam (Quantel  
 200 Brilliant,  $\lambda_d = 532$  nm, 4 ns pulse duration,  $100\text{ mJ cm}^{-2}$  fluence, 10 Hz repetition rate) focused to a  $0.07$   
 201  $\text{mm}^2$  spot on the surface. The desorbed compounds form a gas plume expanding in the vacuum normally  
 202 to the sample surface, and are ionized by an orthogonal UV laser beam (Quantel Brilliant,  $\lambda_i = 266$  nm,  
 203 4 ns pulse duration, 10 Hz repetition rate,  $0.3\text{ J cm}^{-2}$  fluence). At this ionization wavelength, a high  
 204 sensitivity is achieved for PAHs through a resonance enhanced multiphoton ionization process 1+1 REMPI  
 205 (Zimmermann et al., 2001; Haefliger and Zenobi, 1998; Thomson et al., 2007). The generated ions are then  
 206 RF-guided to a He collision cell for thermalization and subsequently mass analyzed in a reflectron time of  
 207 flight mass spectrometer (ToF-MS). A high sensitivity for aliphatic compounds was achieved with a similar  
 208 instrument where the desorbed plume is ionized by a single photon ionization (SPI) process at  $\lambda_i = 118$  nm.  
 209 The ninth harmonic of the Nd:YAG laser is generated in a coherent nanosecond source by frequency-tripling  
 210 of a 355 nm pump beam (Continuum Surelite, 10 ns, 10 Hz) in a low-pressure Xe cell (Popovicheva et al.,  
 211 2017).

## 212 *Secondary Ion Mass Spectrometry*

213 The particles were also analyzed with a commercial IONTOF TOF.SIMS<sup>5</sup> secondary ion mass spectrometer  
 214 (SIMS) with maximum resolving power of  $m/\Delta m \sim 10\,000$ . The sample is placed on a holder and introduced  
 215 into a vacuum chamber with residual pressure of  $\sim 10^{-7}$  mbar. The surface of the sample is probed by a  $\text{Bi}_3^+$   
 216 pulsed ion beam at 25 keV. The primary ion source delivers a pulsed current of 0.3 pA. The penetration  
 217 depth of the primary ions is typically 1-3 nm. In the static mode, used for the surface molecular analysis,  
 218 the ion dose is limited to a level at which every primary ion should always hit a fresh area of the sample. A  
 219 small fraction of the ejected atoms/molecules are ionized (secondary ions) and can thus be analyzed using a  
 220 time of flight tube (V mode). Mass spectra are recorded in both positive and negative polarities, to obtain  
 221 the maximum amount of information on the sample (Irimiea et al., 2018, 2019).

## 222 *2.4. Theoretical model*

223 The model-based workflow (Lee et al., 2019) simulates the in-cylinder gas phase and particulate produced  
 224 in the engine and up to the sampling stage. There are two stages in the workflow: i) calibration of the in-  
 225 cylinder pressure and engine-out emissions using a Stochastic Reactor Model (SRM), and ii) investigation  
 226 on the formation of organic carbons in the sampling stage using a reactor network model.

## 227 *SRM Engine Suite for in-cylinder combustion*

228 The SRM is described by the probability density function (PDF) transport equation and it is assumed  
 229 that the inhomogeneity is described by the distribution represented by the PDF everywhere. The multi-  
 230 dimensional PDF transport equation is represented by an ensemble of  $N_{\text{par}}$  stochastic parcels. Each stochas-  
 231 tic parcel is described by a collection of gas phase species mass fraction and a temperature, i.e.

$$(Y_1^{(i)}, \dots, Y_{N_S}^{(i)}, T^{(i)}) \quad (2)$$

232 where the superscript indices are labels for the parcels (up to  $N_{\text{par}}$ ) and  $N_S$  is the number of species  
 233 considered in the gas phase chemical mechanism. These quantities evolve through a number of processes,  
 234 e.g. chemical reaction, turbulent mixing, flame propagation, wall impingement etc. (Bhave and Kraft, 2004;  
 235 Etheridge et al., 2011; Smallbone et al., 2011; Lai et al., 2018). More detailed information on the application  
 236 of the SRM in a GDI context can be found in Lee et al. (2019).

237 In addition to the gas phase composition and temperature, each parcel contains a particle population  
 238 that consists of soot and inorganics. This model is directly coupled with the gas phase chemistry and a  
 239 three-dimensional type-space is used to describe the particles:

$$P = (m, n_{\text{prim}}, Y_{\text{SOF}}) \quad (3)$$



240 where  $m$  is the particle’s mass,  $n_{\text{prim}}$  is the number of primary particles and  $Y_{\text{SOF}}$  is the mass fraction of  
 241 soluble organic fractions (SOF). The particle population evolves through inception from aromatics from the  
 242 gas phase, surface growth, oxidation, and aggregation. The sectional method is used to solve the population  
 243 balance model.

### 244 Reactor network model for the dilution stage

245 The engine-out composition, both gas and particulate phases, is passed onto a reactor network model to  
 246 mimic the dilution process in the Dekati FPS 4000 diluter described in Section 2.1. The reactor network  
 247 model is illustrated in Fig. 2. R1 and R3 represent the hot (180°C) and cold dilution (35°C) stages  
 248 respectively, whereas R2 and R4 represent the piping connections. The model simulates a population of  
 249 particles with the type space described by Eq. 3. From here, they can be post-processed to give particle  
 250 size distributions, PN, PM and size-resolved SOF mass fractions. The outputs from the reactor network  
 251 model are then compared with measurement data, which include particle size distributions and size-resolved  
 252 chemical particle characterization.

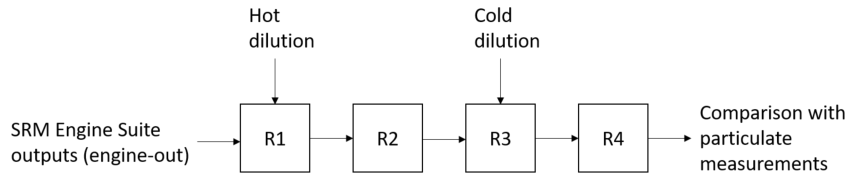


Figure 2: Reactor network model for the Dekati FPS 4000 diluter.

## 253 3. Results and Discussion

### 254 3.1. LII measurements within the exhaust duct

255 The LII technique was used in this work to monitor the evolution of the soot volume fraction (proportional  
 256 with the LII peak signal, see section 2.2) upon various engine regimes. Fig. 3a shows the evolution of the  
 257 LII signal ( $f_\nu$ ) with five engine set points. One can clearly see that the main parameter inducing a strong  
 258 effect on the soot volume fraction is the timing of injection, leading to a 150-fold increase between the **NH**  
 259 (270 deg. BTDC, see Table 2) and the **EI2** (311 deg. BTDC) regimes. This trend is correlated with the  
 260 occurrence of pool fires (*i.e.* liquid fuel burning on the top of the piston) observed only for the points  
 261 **EI1** and **EI2** using endoscopic imaging of the combustion chamber. This observation is consistent with  
 262 the ones revealed by Velji et al. (2009) who experimentally identified that the main source of soot in the  
 263 homogeneous combustion in a gasoline engine is due to the pool fires, while in the stratified mode the soot  
 264 may also originate from local rich regions in the combustion chamber. Bardi et al. (2019) also observed  
 265 a correlation between the occurrence of pool fires and the large increase in soot particle number. On the  
 266 other hand, a moderate increase (by a factor of 3.2) is recorded when the indicated mean effective pressure  
 267 (IMEP) quadruples, from 3 (**NS**) to 12 bar (**NH**). This is consistent with the work of Wang et al. (2014)  
 268 who suggested that this trend could be due to slightly longer combustion duration for a clean injector.

269 In addition to the control of the soot volume fraction, time-resolved LII measurements can provide  
 270 qualitative information about the size of the emitted particles. The LII signal time decays exhibit significant  
 271 variations depending on the engine regime (see Fig. 3b). The “normal regimes” (**NS**, **NM**, **NH**) show  
 272 similar decay times (*i.e.* relatively low influence of the IMEP on the particle size), whereas the non-optimal  
 273 engine operation conditions (early injection, **EI1** and **EI2**) clearly show longer decay times *i.e.* larger  
 274 primary particle sizes. The interpretation of these time-resolved LII decays in terms of soot primary particle  
 275 diameter requires complex energy transfer modeling (Michelsen et al., 2007) which is beyond the scope of  
 276 this work. This modeling is made even more difficult because size distributions of the particles are expected  
 277 to be bimodal. Wang et al. (2014) measured on-line the size distributions of the particles in different GDI  
 278 conditions by scanning mobility particle sizing (SMPS) and highlighted that most of the electrical mobility

279 diameter distributions were bimodal. Particularly they showed that the smallest nucleation mode particles  
 280 could be prevalent in some engine conditions. Providing that LII modeling is undertaken, the coupling of  
 281 LII with EEPS or SMPS offers promising perspectives. Indeed, in case of bimodality (which can be revealed  
 282 by SMPS or EEPS), the LII could provide the diameter of the largest primary particles. The extraction of  
 283 the primary particle diameter from the LII decays, even biased towards the largest ones, could give real-time  
 284 access to this important characteristic without resorting to the use of off-line analyses (by e.g., TEM).

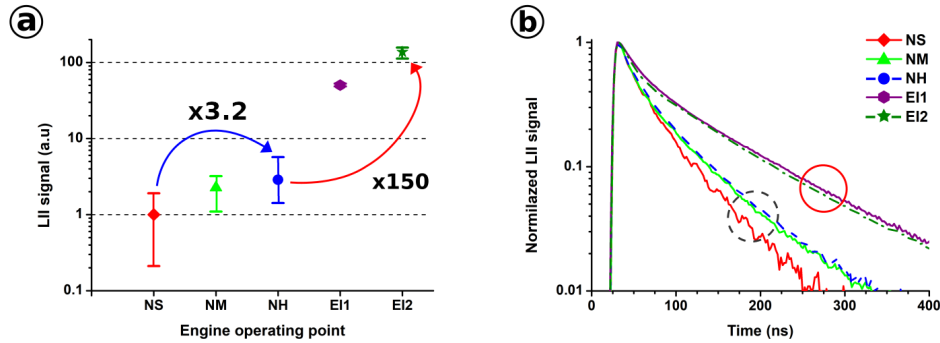


Figure 3: (a) LII peak signal (a.u.) measured at different engine set-points; (b) time-resolved LII signal.

285 These observations provide precious information for optimizing the simultaneous sampling of the par-  
 286 ticulates for off-line analyses. Further efforts will be devoted to calibrate  $f_{\nu}$  using an extinction technique  
 287 at a given engine set-point (Betrancourt et al., 2019) and to combine LII with particle sizers as mentioned  
 288 above in a context of very small particles (down to 10 nm). From the LII measurements, several set-points  
 289 showing a high stability have been selected for the off-line characterization, Table 2.

### 3.2. Structure and morphology

291 A significant challenge in collecting and studying combustion-generated particles is avoiding the agglom-  
 292 eration of the smallest ones during sampling. As small particles are the focus of this work, proper sampling  
 293 is crucial to avoid the aggregation of small particles that would result in their collection on a different im-  
 294 paction stage (with a higher cut-off size compared to the dimensions prior to aggregation). Several samples  
 295 of particles are analyzed with SEM, Fig. 4, in order to ensure that our experimental setup is able to sample  
 296 and collect small primary particles. The particles are collected on Au-coated Si wafers with the Nano-DMA,  
 297 set to a mobility diameter of  $18 \pm 5$  nm (see Section 2.1).

298 One can see that the samples (obtained in different engine regimes) contain predominantly single, spher-  
 299 ical particles with a diameter ranging from 17 to 23 nm, Fig. 4, and are presumably primary soot particles.  
 300 This is in agreement with previous studies on the emitted particles from GDI engines (Gaddam and Wal,  
 301 2013; Price et al., 2007). The fact that primary particles were successfully sampled indicates that the ex-  
 302 perimental setup is working as intended, minimizing the aggregation of particles to an extent that should  
 303 not affect the subsequent chemical analysis.

304 AFM analysis is performed on samples collected in the **NH** engine regime (optimal conditions, high  
 305 load), Table 2. The technique is used to determine the distribution and the size of single particles. AFM  
 306 measurements are performed on a  $1.2 \times 1.2 \mu\text{m}$  region ( $300 \times 300$  pixels), Fig. 5a. The heights of particles 1  
 307 and 2 were determined to be 10 nm and 6 nm, Fig. 5d. The measured diameter is highly dependent on the  
 308 used tip, especially when the radius of the scanned object is close to the one of the tip. The Full Width at  
 309 Half Maximum (FWHM) diameters of particles 1 and 2, obtained with a sharp tip ( $r=1$  nm), are  $<48$  nm  
 310 and  $<43$  nm, respectively.

311 Two smaller zones have been characterized by TERS with a resolution of 7 nm/pixel (zone I) and 5  
 312 nm/pixel (zone II) and with a Raman integration time of 100 ms (one spectrum/pixel). The TERS maps  
 313 of zones I and II are presented in Fig. 5b and 5c, respectively. Raman spectra of carbon materials contain  
 314 two main features (see Fig. S2 in Supplementary Material): the G band, derived from in-plane motion of  
 315 carbon atoms (around  $1580 \text{ cm}^{-1}$ ) and the D band (D1), attributed to lattice motion away from the center

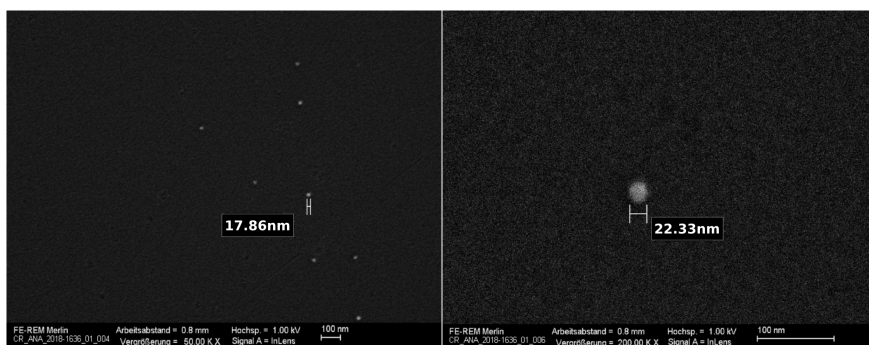


Figure 4: SEM images of size-selected particles (size bin centered at 18 nm) collected with a NAS in the **NH** (left panel) and **NM** (right panel) engine operating regimes.

316 of the Brillouin zone (around  $1270 - 1450 \text{ cm}^{-1}$ ). The TERS maps displayed in Fig. 5b,c are obtained by  
 317 integrating the G band only.

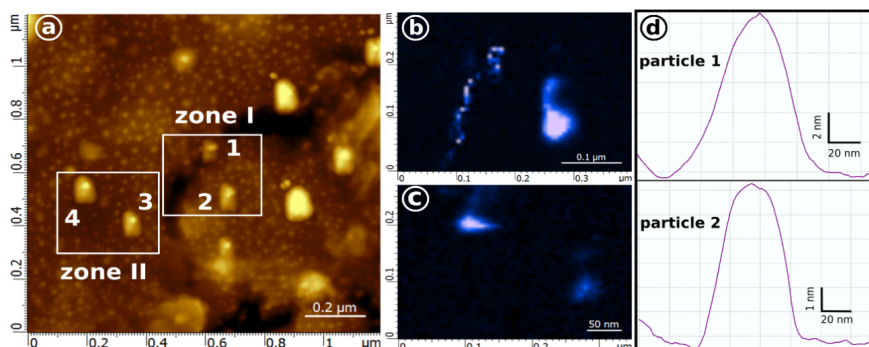


Figure 5: AFM and TERS study of nanoparticles collected in the **NH** engine regime (optimal conditions, high load). Topography image ( $1.2 \times 1.2 \mu\text{m}$ ) (a), TERS mapping of zone I, particles 1 and 2 (b), and zone II, particles 3 and 4 (c), topographic cross-section of particles 1 and 2 (d).

318 Besides TERS maps, TERS spectra were obtained for particles 2, 3, and 4 and are displayed in Fig. S2.  
 319 The three spectra (Fig. S2) exhibit very different profiles (for example, the relative intensity of the D band  
 320 to the G band is higher for particle 2 and lower for particles 3 and 4) which is indicative of major structural  
 321 variations between particles collected in the same engine regime and the same size bin. A more quantitative  
 322 approach involves a five-band fitting method, often applied to Raman spectra of soot particles (Sadezky  
 323 et al., 2005; Parent et al., 2016), in which the G, D1, D2, and D4 bands are fitted with a Lorentzian profile,  
 324 whereas the D4 band is fitted with a Gaussian profile. The fit results are presented in Fig. S2. The spectral  
 325 parameters determined by curve fitting are highly variable across the three particles (Table S1), confirming  
 326 our first observation. For instance, the ratio of the integrated areas of D1 to those of (G+D2) bands is  
 327 usually considered as a good indicator of the order in the soot structure (Carpentier et al., 2012). This value  
 328 increases from 1.5 (particle 4) to 2.5 (particle 3) and to 3 (particle 2), suggesting that particle 2 has a much  
 329 more disordered structure compared to particles 3 and 4. In addition, the presence of strong signatures at  
 330  $1208$  and  $1278.6 \text{ cm}^{-1}$  on the spectra of particles 3 and 4 could be an indicator of organic molecules present  
 331 on the surface of the particles.

332 These TERS measurements, performed (to the best of our knowledge) for the first time on ultra-fine  
 333 combustion-generated particulate matter, reveal the diversity (at least in terms of nanostructure) of soot  
 334 particles generated by the same engine, operating in the same conditions, and collected in the same size  
 335 bin. This observation is of paramount importance for the interpretation of our off-line chemical composition  
 336 measurements discussed in section 3.3, which, conversely, do not probe individual particles but rather a  
 337 high number of them because of the diameter of the laser or ion beam used in the experiments. Therefore,

338 the properties and trends we derive in section 3.3 are averaged over many (different) particles making them  
339 statistically significant. These trends offer valuable input for the theoretical model, also operating with  
340 statistical approaches on particles ensembles.

### 341 3.3. Chemical characterization

342 To obtain a comprehensive chemical characterization and thus provide valuable inputs for building and  
343 validating the theoretical model, size-selected particles are analyzed with L2MS and SIMS. Data-treatment  
344 was performed according to our recently developed comprehensive methodology (Irimiea et al., 2018, 2019;  
345 Duca et al., 2019) which includes powerful statistical techniques such as PCA and HCA. Since the particles  
346 emitted in a certain engine regime are size-selected, a notation scheme that indicates the size of collected  
347 particles, in addition to the engine regime will be used from here forth ( $\langle \text{engine regime} \rangle : \langle \text{upper size} \rangle$   
348  $\langle \text{lower size limit} \rangle$ ), e.g. **OM:180-100**. Due to a low particle coverage, the substrate (Al foil) was  
349 also probed which led to the formation of  $\text{Al}^+$  and  $\text{Al}_2\text{O}^+$  ions, detected at  $m/z$  27 and 70, respectively.  
350 Consequently, even though the presence of Al compounds in such samples is typically a marker of engine  
351 wear, these peaks will rather be associated with the aluminum substrate in our case.

#### 352 3.3.1. Size discrimination

353 One of the major points that need to be determined is whether the chemical composition of emitted  
354 particles varies with their size. On that ground, size-selected particles produced in two different engine  
355 regimes (**OM** – optimal conditions with an addition of oil, and **EM** – low air/fuel ratio) have been analyzed.  
356 These particular engine regimes were chosen as they simulate two completely different malfunctions, *i.e.*  
357 extreme cases of operation, equivalent to either a “worn out” engine with high oil consumption (**OM**) or  
358 a fault in the fuel system with a normal oil consumption (**EM**). This information, along with similar  
359 analyses performed on size-selected particles emitted in other operation conditions, allows for a more precise  
360 calibration of the MGA.

#### 361 “Worn out” engine (**OM** regime)

362 The analysis of samples obtained in the **OM** regime (optimal conditions, addition of oil) was performed  
363 with two-step laser mass spectrometry with two different ionization wavelength (266 nm and 118 nm), thus  
364 enabling us to selectively target either aromatic or aliphatic compounds. Several metals were detected ( $\text{Na}^+$ ,  
365  $\text{K}^+$  and  $\text{Ca}^+$ ) with both ionization wavelengths. While  $\text{Na}^+$  and  $\text{K}^+$  are mostly associated with fuel, they  
366 can also be present in the lubricating oil as trace elements (Huang et al., 1994; Cadle et al., 1997; Cross  
367 et al., 2012; Dallmann et al., 2014). In addition, the origin of  $\text{Ca}^+$  is most likely the lubricating oil, since  
368 Ca is a component of detergent additives, widely used in modern motor oils (Cadle et al., 1997; Dallmann  
369 et al., 2014). Mostly aromatic species are detected when the ionization of laser-desorbed compounds is  
370 performed at 266 nm (Fig. 6). They are visually separated into two groups: one of lower and one of higher  
371 mass compounds. The first group is comprised of aromatic species with one to two aromatic rings and their  
372 alkylated derivatives ( $m/z$  78 – 170) and is present in the spectra of all the samples with varying relative  
373 intensities. The second group is composed of aromatic compounds with three and more rings. According  
374 to Bari et al. (2010), the first group can be considered as volatile species, as they are mostly present in the  
375 gas phase. The second group is comprised of semi and non-volatile compounds. Therefore, the intensity  
376 ratio of the first to the second group is related to the overall volatility of the organic layer on the surface  
377 of particles. Species with masses between  $m/z$  178 and 398 are detected on larger **OM** particles (180 – 32  
378 nm), *i.e.* on samples **OM:180-100**, **OM:100-56**, and **OM:56-32**, while for the sample **OM:32-18** (32 –  
379 18 nm) the highest detected mass is only  $m/z$  278. [Table S2 displays the assignment of the most intense mass peaks recorded by L2MS with two different ionization wavelengths \(256 nm and 118 nm\).](#)

380  
381 The intensity ratio of species belonging to the second group to those in the first one changes from sample  
382 to sample, within the **OM** regime. For the largest particles (**OM:180-100**) as well as for the smallest  
383 (**OM:32-18**), the first group ( $78 \leq m/z \leq 170$ ) shows a higher intensity. However, for samples **OM:100-56**  
384 and **OM:56-32**, the second group ( $m/z \geq 178$ ) exhibits a higher contribution. Within the first group, for all  
385 the samples the base peak is located at  $m/z$  128 and the group features fairly constant peak and intensity

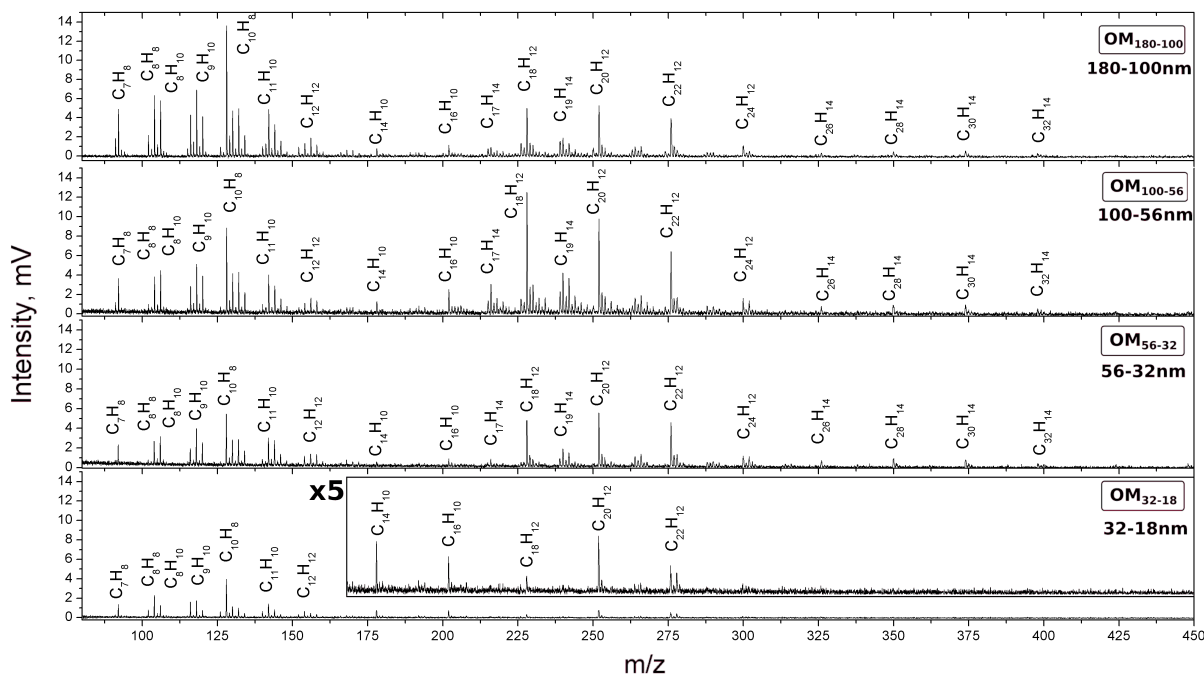


Figure 6: L2MS spectra of four samples (particle size 180-18 nm) obtained in the **OM** engine conditions (optimal operation, medium load). The analyses were performed with an ionization wavelength  $\lambda_i=266$  nm to target aromatic compounds.

[New figure](#)

distributions. The second aromatic group shows a distinct behavior, where the base peak is  $m/z$  252 for samples **OM:180-100**, **OM:56-32**, and **OM:32-18**, but  $m/z$  228 for sample **OM:100-56**. However, with the exception of the peak at  $m/z$  228, peak and intensity distributions change only slightly from sample to sample. The change in the relative intensity of the  $m/z$  228 peak is probably linked to a  $C_{18}H_{12}^+$  isomer present on particles in the size range 100 – 32 nm. The fact that only species up to  $m/z$  278 can be seen on sample **OM:32-18** might be explained by an overall lower intensity, as this sample had the lowest coverage of deposited particles. However, since the contribution from the highest masses (*e.g.*  $m/z \geq 275$ ) does not exceed a few percent of that given by the whole distribution of aromatic compounds making up the second group ( $\geq 3$ -ring aromatic compounds), we can still derive the intensity ratio of species from the second group to those belonging to the first one. A low ratio observed for this sample suggests that smaller particles contain mostly light aromatic species.

The samples also contain a variety of aliphatic species, detected with a different ionization scheme ( $\lambda_i=118$ nm)(Popovicheva et al., 2017), Fig. S3. Ion series with the formula  $C_nH_{2n-1}^+$  is typical of cycloalkanes and alkenes while the  $C_nH_{2n+1}^+$  series (alkyl fragments) is typical of linear or branched alkane compounds (McLafferty and Tureek, 1993). The series at  $m/z$  67, 81, 95, and 109 ( $C_nH_{2n-3}$  fragments of bicycloalkanes) is also present, however with a very low intensity. The asymmetrical shape of the peaks is a sign of fragmentation. The fragmentation pattern is characteristic of the presence of aliphatic hydrocarbons, alkanes ( $C_nH_{2n+2}$ ). As alkane cations are not stable, especially if the excess internal energy is high after ionization, they can easily fragment. Since lubricating oils tend to be dominated by cycloalkanes due to the deliberate removal of *n*-alkanes during a de-waxing process (Tobias et al., 2001), an intense signal for cycloalkanes is usually a sign of oil contribution. The main source of aliphatic compounds can be derived from the ratio of *n*-alkanes to cycloalkanes. The signal corresponding to alkanes is superior to that of neighboring cycloalkanes in the mass range  $m/z = 67 - 71$  and  $81 - 85$  when the fuel is the main source of these compounds, and inferior for the lubricating oil (Dallmann et al., 2014; Sakurai et al., 2003; Tobias et al., 2001). Ion signals at  $m/z$  71 and 85 are lower than signals at  $m/z$  69 and 83, suggesting that the measured exhaust particles mainly consist of unburnt lubricating oil (in case of diesel particles this pattern

412 would be caused by at least 95% oil and 5% fuel, while in the case of gasoline, the ratio should be higher  
 413 (Dallmann et al., 2014; Sakurai et al., 2003). The one exception is observed for the sample **OM:100-56**  
 414 where the signal at  $m/z$  69 is lower than that of  $m/z$  71 ( $r = S_{69}/S_{71} \approx 0.8$ ), while the  $m/z$  83 to 85 ratio  
 415 is close to unity. Since the source of organic species in the exhaust includes fuel, lubricating oil, and their  
 416 partially oxidized products, it is possible that particles containing the most unburnt fuel are concentrated  
 417 in the size bin associated with sample **OM:100-56** (100 – 56 nm) and decreases towards both smaller and  
 418 larger particles. Peaks at  $m/z$  50, 64, 66 and 78 can be attributed to fragments of aromatic species. Series  
 419 of highly unsaturated aliphatic compounds are present as well:  $C_{2n}H_2^+$  and  $C_{2n}H_4^+$ . These series were at-  
 420 tributed to polyynic fragments, known to be present in rich premixed flames and play an important role in  
 421 the formation of combustion-generated particles (Hansen et al., 2008; Li et al., 2009).

422 To classify the samples and uncover differences and similarities between them, principal component  
 423 analysis (PCA) was used (Irimiea et al., 2018, 2019; Duca et al., 2019). This statistical method is able to  
 424 reduce the number of dimensions of complex mass-spectrometric data, thus increasing its readability, while  
 425 still preserving most of the original information. Before applying PCA, the data was first normalized and  
 426 baseline corrected (Irimiea et al., 2018, 2019; Duca et al., 2019) while all peaks associated with the substrate  
 427 were disregarded. Each principal component (PC) accounts for a defined percentage of the variance within  
 428 the dataset. For both ionization schemes, the first two components are responsible for most of the variation  
 429 between samples (containing particles of different sizes) ( $\approx 97\%$ ), and therefore the number of dimensions  
 430 of the original data was reduced to only two. The contribution of mass peaks to each principal component  
 431 is represented by their loading (Fig. S4), which reflects the interpretation of individual components. To  
 432 extract the maximum amount of information, the data obtained with different ionization wavelengths was  
 433 treated separately. In case of the ionization at 266 nm, the first principal component (PC1) can be associated  
 434 with the total number of different aromatic species, since it receives a high negative contribution from both  
 435 alkylated and non-alkylated PAHs. The first group of aromatic compounds ( $78 \leq m/z \leq 170$ ) shows a high  
 436 positive contribution to the second principal component (PC2) while the second group ( $m/z \geq 178$ ) is related  
 437 to the negative PC2 value. For the data obtained with 118 nm ionization, PC1 is linked to all detected  
 438 aliphatic species and can be also seen as an indicator of the homogeneity of aliphatic signal throughout the  
 439 mass spectrum. PC2 has a strong contribution from highly unsaturated hydrocarbons ( $C_{2n}H_2^+$ ,  $C_{2n}H_4^+$ ,  
 440 positive PC2) and several aliphatic species (negative PC2), Fig. S4. Moreover, since contributions to  
 441 PC2 from  $C_{2n}H_2^+$ ,  $C_{2n}H_4^+$ , and aliphatic species ( $C_nH_{2n-1}^+$ ,  $C_nH_{2n}^+$ ,  $C_nH_{2n+1}^+$ ) have the opposite sign, PC2  
 442 represents the ratio of highly unsaturated hydrocarbons to aliphatic species. In addition, the fact that peaks  
 443 at  $m/z$  50, 52, 74 and 78 (fragments of aromatic species) have a high contribution to PC2 proves that these  
 444 species have the same origin, which is in agreement with soot formation models (Hansen et al., 2008; Li  
 445 et al., 2009).

446 Data in terms of PC1 and PC2 for both ionization wavelengths are presented in Fig. 7. There is a  
 447 notable separation between different samples, thus demonstrating the capability of the PCA method to  
 448 discriminate between samples that present, at first glance, similar mass spectra. Data points for each  
 449 sample are clustered together, proving that the sample surface is homogeneous and the reproducibility of  
 450 the method is high. Sample **OM:180-100** contains a large number of aromatic species (266 nm ionization),  
 451 with a higher contribution coming from the light-weight compounds ( $78 \leq m/z \leq 170$ ). In contrast, sample  
 452 **OM:100-56** exhibits a higher contribution from the second group of aromatic compounds ( $m/z \geq 178$ ).  
 453 Sample **OM:56-32** seems to have fewer species, however heavier compounds ( $m/z \geq 178$ ) still dominate. For  
 454 the smallest analyzed particles, *i.e.* sample **OM:32-18**, the contribution of lighter aromatic compounds  
 455 increases considerably, with only a few species detected from the second group. It appears that aromatic  
 456 species with a lower mass are present on all samples and are not bound to a specific particle size. In contrast,  
 457 there is a clear increase in the contribution from higher mass aromatic species for **OM:100-56** and **OM:56-**  
 458 **32** samples, suggesting that these compounds preferably adsorb on particles in this size range (100 – 32  
 459 nm). Sample **OM:100-56** shows the most peaks coming from aliphatic species (118 nm ionization), including  
 460 peaks in the mass range  $m/z$  64 – 112 (which reflects as a negative PC1, the latter being representative of  
 461 all detected aliphatic species in Fig. 7). The smallest number of aliphatic compounds were detected on the  
 462 **OM:56-32** sample which also has a fairly inhomogeneous-looking spectrum (Fig. S3). The contribution of  
 463 highly unsaturated hydrocarbons ( $C_nH_2^+$  and  $C_nH_4^+$ ) decreases with the size of particles, being the highest

464 for the **OM:32-18** sample and the lowest for the **OM:180-100**, positive PC2. At the same time, the  
 465 contribution of other aliphatic compounds increases with the particle size.

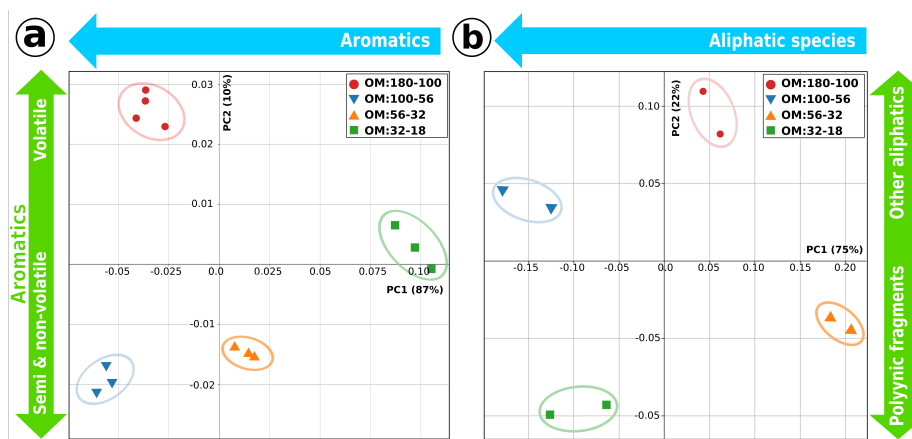


Figure 7: Size separation of combustion-generated particles obtained in the **OM** engine regime (optimal operation with addition of oil, medium load) by means of principal component analysis, with ionization wavelengths of  $\lambda_i=266$  nm (a), or  $\lambda_i=118$  nm (b). Species were classified as volatile, semi- and non-volatile compounds according to Bari et al. (2010).

#### 466 Fuel system failure (**EM** regime)

467 Another engine regime that simulates a malfunction is **EM** (low air/fuel ratio, medium load), which acts  
 468 as one more extreme operation point, this time with a normal oil consumption. Particle emissions obtained  
 469 in this engine regime are analyzed with SIMS in both positive and negative polarity (Fig. S5 and Fig. S6,  
 470 Table S3 contains all the detected peaks in both polarities). Metallic and metalloid ions such as  $\text{Na}^+$ ,  $\text{Mg}^+$ ,  
 471  $\text{Al}^+$ ,  $\text{Si}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^+$  and  $\text{Cu}^+$  are present, however, their intensity is higher for the blank aluminum foil, and  
 472 therefore they will be assumed to be coming from the underlying substrate rather than from the collected  
 473 particles. All spectra obtained in the positive polarity are dominated by hydrocarbon fragments  $\text{C}_n\text{H}_m^+$ .  
 474 Masses between  $m/z$  128 and 300 can be mostly attributed to PAHs. Additional minor signals correspond  
 475 to  $\text{NH}_4^+$  and oxygenated species such as  $\text{CH}_3\text{O}^+$  ( $m/z$  31),  $\text{C}_2\text{H}_4\text{O}_2^+$  ( $m/z$  60) and  $\text{CHO}_4^+$  ( $m/z$  77).  
 476  $\text{CH}_3\text{O}^+$  can be associated with methyl esters or ethers. Alternatively, it can correspond to primary alcohols  
 477 or methyl-carbinols. The oxygenated positive ions,  $\text{CH}_3\text{O}^+$  and  $\text{C}_2\text{H}_4\text{O}_2^+$  present the highest correlation ( $R$   
 478  $= 0.98$ ) between the integrated areas of their peaks (normalized with respect to total ion count, TIC), thus  
 479 indicating a common source. For instance, isopropanol, which is used as a gas dryer additive in gasoline  
 480 for fuel system protection (Patil et al., 2014), could be a common source for these two ions. Ferrocene  
 481 ( $\text{Fe}(\text{C}_5\text{H}_5)_2$ ) is believed to be present in the fuel, since its fragment ( $\text{FeC}_5\text{H}_5^+$ ) was detected. Ferrocene  
 482 is sometimes used as a fuel additive that acts as an antiknock agent. Hopanes and n-alkanes ( $\text{C}_{26} - \text{C}_{36}$ )  
 483 were also detected, they are believed to be linked to unburned lubricant oil (Wang et al., 2009). The high  
 484 correlation between these peaks ( $R = 0.85 - 0.98$ ) also suggests a common source. The correlation between  
 485 PAHs and hopanes is almost non-existent, therefore we can conclude that PAHs are formed during the  
 486 combustion process and are not remnants of oil/fuel. Negative SIMS spectra, as presented in Fig. S6, are  
 487 dominated by  $\text{H}^-$ ,  $\text{O}^-$ , and  $\text{OH}^-$  fragments. Additional strong features correspond to the  $\text{C}_n^-$  and  $\text{C}_n\text{H}^-$   
 488 ( $n = 1 - 9$ ) series with the hydrogenated carbon cluster  $\text{C}_n\text{H}^-$  being more intense compared to  $\text{C}_n^-$  when  $n$   
 489 is an even number (except in the case of  $n = 1$ ).  $\text{C}_n^-$  ( $n = 2 - 4$ ) fragments are considered to be a marker  
 490 for elemental carbon (EC) in aerosol mass spectrometry (AMS) data (Pagels et al., 2013). The fact that  
 491 detected carbon clusters have the same source is confirmed by the high positive correlation factors between  
 492  $\text{C}_2^-$ ,  $\text{C}_3^-$ , and  $\text{C}_4^-$ . The correlation between  $\text{C}_3^-$  and  $\text{C}_4^-$  is the highest ( $R_{max} = 0.95$ ), while the lowest  
 493 is between  $\text{C}_2^-$  and  $\text{C}_4^-$  ( $R_{min} = 0.74$ ).

494 All samples can be easily separated by PCA, Fig. S7, and by hierarchical clustering analysis (HCA),  
 495 Fig. 8. For the PCA, the first two principal components account for 92% and 95% of the total variation

496 within the data obtained in the positive and negative polarity, respectively. For the positive polarity, the  
 497 first principal component receives a high negative contribution from aliphatic compounds ( $C_nH_{2n-1}^+$  and  
 498  $C_nH_{2n+1}^+$ , negative PC1), while other aliphatic species show a positive contribution. PC2 can be seen as the  
 499 ratio of aliphatic species (positive PC2) to aromatic compounds, such as PAHs and their fragments (negative  
 500 PC2 value). For the negative polarity, PC1 is related to the ratio of the amount of oxygenated species to the  
 501  $C_n^-$ ,  $C_nH^-$  family (with a positive PC1 contribution linked to a high fraction of oxygenated species while  
 502 a negative PC1 value indicates a high amount of  $C_n^-$ ,  $C_nH^-$ , *i.e.* a high EC). PC2 is linked to oxygenated  
 503 species (positive for hydrocarbon-based compounds and negative for oxygenated species containing S, P  
 504 and N). From Fig. S7, it is clear that PCA can easily distinguish between samples, implying that size-  
 505 selected particulates are also chemically different in the EM regime. It clearly shows that aliphatic species  
 506 are concentrated predominantly on samples **EM:180-100**, **EM:56-32**, and **EM:32-18** and that aromatic  
 507 compounds are present in comparable amounts on the lower four stages, 100 – 10 nm particle size (**EM:100-  
 508 56**, **EM:56-32**, **EM:32-18** and **EM:18-10**). Samples **EM:100-56**, **EM:56-32**, and **EM:32-18** (100 – 18  
 509 nm size range) exhibit the highest amount of  $C_n^-$  and  $C_nH^-$  ions, and therefore have a high EC content.  
 510 Sample **EM:180-100** has the highest contribution from oxygenated compounds that contain elements other  
 511 than carbon and hydrogen (*e.g.*  $PO_3^-$ ,  $SO_3^-$ ,  $SO_4^-$ ,  $PO_4^-$ ,  $NaSO_4^-$ ), while samples **EM:100-56** and  
 512 **EM:18-10** contain the lowest. Eventually, negative polarity SIMS data extracted from EM samples (Fig.  
 513 S7) can be divided into three main clusters according to the amount and nature of oxygenated species present  
 514 on the samples. Specifically, the first cluster encompasses the two samples which exhibit the most oxygenated  
 515 species, *i.e.* **EM:100-56** and **EM:18-10**. The second cluster gathers the two samples which bear much  
 516 less oxygenated species compared to the others, along with more elemental carbon, *i.e.* **EM:56-32** and  
 517 **EM:32-18**. Lastly, the third cluster is sample **EM:18-10**, which contains the most inorganic oxygenated  
 518 species of all samples.

519 HCA is a statistical technique able to group samples according to the distance between them in a  
 520 multidimensional space while also accounting for the total variance within the dataset (Rencher, 2000; Pei  
 521 et al., 2008). The distances between the samples are represented in form of a dendrogram, Fig. 8. We can  
 522 see that samples **EM:180-100**, **EM: 56-32**, and **EM:32-18** form a relatively small cluster (small distance  
 523 between data-points), thus indicating their similarity. Likewise, **EM:100-56** and **EM:18-10** samples are  
 524 grouped together hence forming a second cluster, well separated from the first one. Samples in these two  
 525 clusters are thus very different, primarily due to the high contribution of  $C_nH_{2n-1}^+$  and  $C_nH_{2n+1}^+$  ions  
 526 to **EM:100-56**, and **EM:18-10** samples (as already shown by PCA). Interestingly, the distance between  
 527 the blank and the second cluster (**EM:100-56** and **EM:18-10** samples) is relatively small, which can be  
 528 explained by the lower coverage of these samples.

### 529 3.3.2. Source discrimination

530 We showed in section 3.3.1 that some chemical compounds of different provenience are preferentially  
 531 found on particles featuring a distinct size range. It is now possible to determine the contribution of  
 532 major sources to the formation of particulates. Determining the impact of various sources to the chemical  
 533 composition of particulates will help further improve the theoretical model. On that basis, samples obtained  
 534 in engine operation regimes (**OM**, **EM**, **NM**, and **NH**) with different contribution from fuel and oil (main  
 535 sources of particulates) are analyzed and compared using PCA.

536 The first two PCA components, PC1 and PC2 (~98%) are presented in Fig. 9. It is clear that particles  
 537 produced in an optimized engine regime (medium and high load) are chemically very different from the ones  
 538 produced in non-optimal ones and, therefore, can be easily separated by their principal components (Fig.  
 539 9a). PC1 alone (~91%) allows the separation of regimes, based on the abundance of aliphatic fragments  
 540 (positive contribution to PC1, Fig. S9). Consequently, samples produced in non-optimal regimes are  
 541 characterized by a higher relative contribution from aliphatic fragment ions compared to optimized engine  
 542 regimes. PC2 is linked to the aliphatic fragment ions and aromatic species (positive PC2 value), however  
 543 some aliphatic fragment ions ( $C_5H_7^+$ ,  $C_5H_9^+$ ,  $C_3H_7^+$ ,  $C_4H_7^+$ ) contribute to the negative value of PC2.  
 544 Data points corresponding to optimal engine regimes form a smaller cluster, implying that particles produced  
 545 in non-optimal conditions exhibit a much larger variability in their chemical composition.



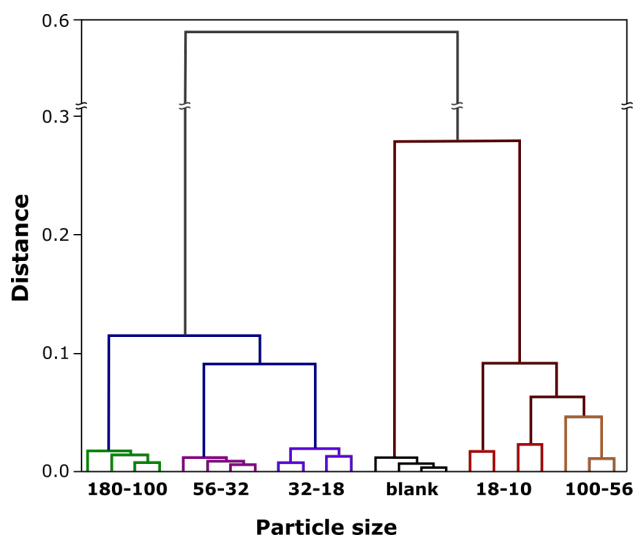


Figure 8: Separation of size-selected particulates obtained in the **EM** (low air/fuel ratio) engine regime by the hierarchical clustering analysis based on positive polarity SIMS spectra.

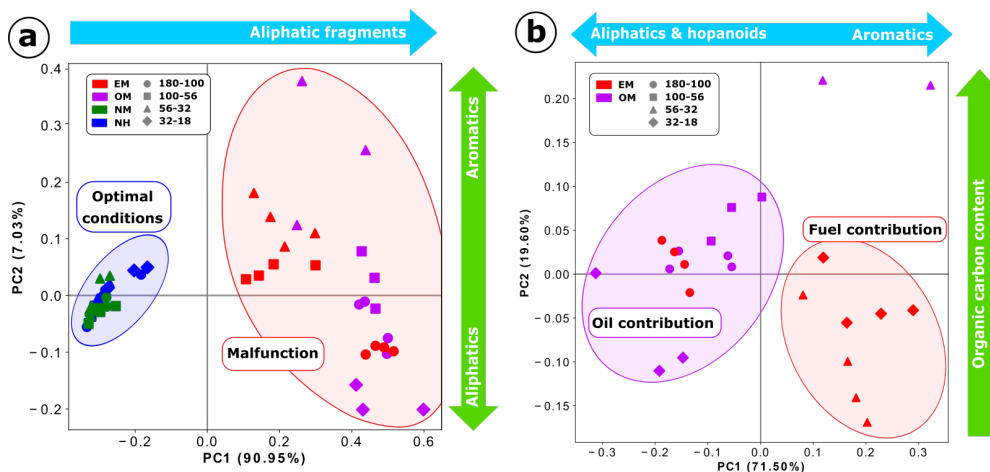


Figure 9: Separation between different engine regimes (a) and main sources of particles (b).

546 The two non-optimal regimes have been compared using the same statistical method, which further  
 547 enables the distinction between the two main contributors to particulate emissions from the internal combustion engine: fuel and oil, Fig. 9b. PC1 ( $\sim 71\%$ ), which is accountable for the separation of the two regimes (and consequently sources), is linked to the contribution of hydrogen-rich hydrocarbons on one side (negative contribution) and to fragment ions and aromatic species on the other (positive contribution, Fig. S9). This reveals that oil-related particles feature more hydrogen-rich hydrocarbons, while an excess of gasoline leads to the production of more aromatic species. The increase in the contribution of fragment ions in the latter is probably linked to the increase in the aromatic contribution, since the majority of fragments can be associated to the fragmentation of PAHs (McLafferty and Tureek, 1993). PC2 ( $\sim 20\%$ ) is associated with the presence of aromatic hydrocarbons, thus confirming that the presence of aromatic species is related to fuel combustion. Two data-points, corresponding to **OM:56-32**, show a rather high contribution from OC, and aromatic compounds in particular, unlike other **OM** samples. Since these compounds are linked to the contribution of fuel, we can infer that, for the **OM** regime, particles in this size (56-32nm) mostly originate from fuel combustion.

### 3.3.3. Influence of the catalytic stripper

We have previously shown the analysis of collected particles from the “raw exhaust” (at the exhaust port), and thus gathered information about the chemical composition of emitted particles that will serve as inputs to test and improve the MGA. However, particles present in the “raw exhaust” contain a multitude of organic species (as is shown above), with various degrees of volatility, and since the current regulations limit only the number of non-volatile particles, one should also study PN emissions after the removal of the volatile fraction. This is especially important in this study as this information will also help characterize and model the catalytic stripper (CS) that will be used to remove volatile compounds in the PEMS measuring system – whose development is the ultimate goal of the PEMS4Nano project. For such a system, volatile removal efficiency of the CS should be in accordance with European regulations, that is to say >99% removal of  $\geq 30$  nm tetracontane ( $\text{CH}_3-(\text{CH}_2)_{38}-\text{CH}_3$ ) particles with an inlet concentration of  $\geq 10000 \text{ cm}^{-3}$  at the minimum dilution (European commission, 2017). However, supplementary efforts are currently being made to better understand how the CS that complies with these regulations affects other individual organic compounds that are commonly present on the surface of combustion generated particles (such as PAHs) – important information for modeling the non-volatile fraction leaving the CS and entering the counting stage of the instrument. To study the influence of the CS, two sets of exhaust particles are collected and subsequently analyzed. One set was sampled with and one without the catalytic stripper. The engine regime was exactly the same for both sets of samples. Here we only show some preliminary results on the influence of the CS to the chemical composition of emitted particles, however, a more complete and detailed study will be presented in an upcoming paper.

From the mass spectra (L2MS) of the two sets we can already see the difference in the absolute intensity of all the peaks corresponding to organic species (considerably smaller for the samples obtained with the catalytic stripper). However, the signal which corresponds to carbon clusters is considerably higher for particulates sampled after the catalytic stripper (Fig. S10). PCA clearly shows that particles sampled with and without the catalytic stripper can be discriminated based on their OC and EC content (PC1). The second principal component is linked to the the organic fraction and small mass carbon clusters ( $\text{C}_{10}^+$  and  $\text{C}_{11}^+$ , positive PC2 value) as well as the contribution from carbon clusters with a higher mass (negative PC2 value), Fig. S11. The catalytic stripper removed the volatile particles as well as the organic species from the nonvolatile core and, as a result, the contribution of EC (carbon clusters) increased, Fig. 10. Accordingly, particles present in the “raw exhaust” have a higher contribution from organic components, Fig. S11. The only exception are the particles in the size range 56-18 nm (**NHC:56-32** and **NHC:32-18**), which might be the result of a combination of (i) a high contribution from organic components to particles in this size-range (as previously shown), and (ii) a lower efficiency of the catalytic stripper in this size-range (Swanson et al., 2013).

Generally, particles sampled with a catalytic stripper are characterized by a weak contribution from organic species and a much high elemental carbon content (linked to the presence of carbon clusters,  $\text{C}_n$ ). From the above preliminary results we can conclude on the effectiveness of the catalytic stripper in removing most of the organic fraction from the surface of the particles.

### 3.3.4. Trends in the chemical composition

A detailed chemical characterization of particulate matter is desirable and can elucidate the soot formation, growth, ageing, and reactivity. However, to facilitate the comparison of mass spectrometric results with other experimental measurements and also support the interaction with modelers that use the data as inputs for various scale simulations, individual compounds are often grouped into classes. Compounds are grouped based on their chemical family (aromatics<sup>+</sup>,  $\text{C}_n\text{H}_{2n-1}^+$ ,  $\text{C}_n\text{H}_{2n-3}^+$ , hopanes<sup>+</sup>, n-alkanes<sup>+</sup>) as well as their connection to the elemental carbon content ( $\text{C}_n^-$ ) (Gilardoni et al., 2007; Kirchner et al., 2003). Moreover, OC can be expressed as the sum of the former groups of organic compounds (Pagels et al., 2013; Delhaye et al., 2017). These chemical families/groups have been chosen as they have different sources and roles in the formation and ageing mechanism of combustion-generated particles (*e.g.* PAHs are associated with the combustion of gasoline, while hopanoid compounds are seen as markers of unburnt lubricating oil). The contribution of a group to a mass spectrum is equal to its normalized intensity (to TIC). As an example, trends in the chemical composition for the **EM** engine regime are illustrated in Fig. 11, where

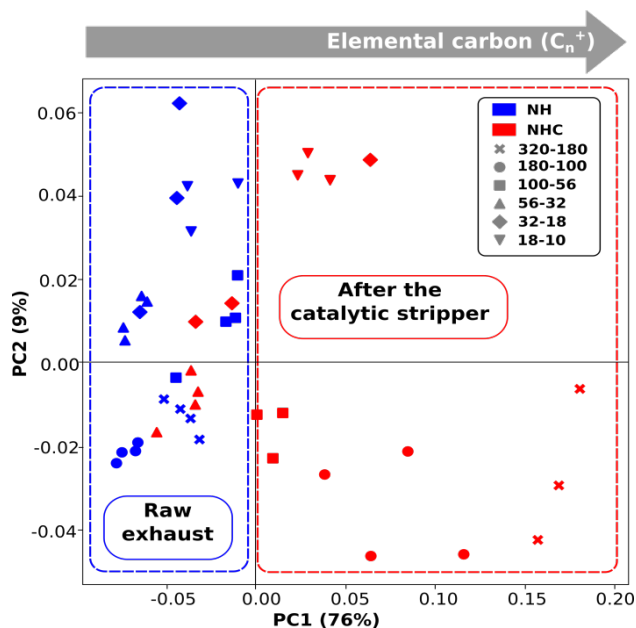


Figure 10: Discrimination between particles sampled from the raw exhaust and after the catalytic stripper.

611 the error bars correspond to the standard deviation associated with multiple zones of each sample. The  
 612 normalized signals obtained for the blank filter are given for comparison. For most of the fragments, relative  
 613 intensities of the blank filter are negligible. The total contribution of aromatic compounds and the  $C_n^-$   
 614 family increases towards sample **EM:32-18**; a similar variation was also found for **NM** and **HM** engine  
 615 regimes. Aliphatic families ( $C_nH_{2n-1}^+$  and  $C_nH_{2n-3}^+$ ) are the most abundant on samples **EM:180-100**,  
 616 **EM:56-32** and **EM:32-18**, when only a small contribution is observed for the other two samples (peak  
 617 intensities comparable to those of the blank aluminum foil). Hopanes and n-alkanes are mostly present on  
 618 sample **EM:180-100** and since they are attributed to the lubricating oil, one can conclude that the unburnt  
 619 oil is found predominantly on bigger particles. This is slightly different compared to the **OM** engine regime  
 620 where the oil contribution is the highest on sample **OM:100-56**. This difference might be linked to the  
 621 state of the oil in the combustion chamber: for the **EM** regime, the oil originates from an oil film present  
 622 on the cylinder liner while for **OM** regime, oil was deliberately added to the combustion chamber, forming  
 623 a mist.

624 The relative abundance of the  $C_n^-$  fragments (markers of the elemental carbon), compared to the TIC in  
 625 the negative polarity SIMS spectra is shown in Fig. 11. The relative proportion of these fragments increases  
 626 from the sample made of the largest particles (180-100 nm) to that holding the smallest ones, reaching  
 627 its maximum for sample **EM:32-18** and then dropping significantly for **EM:18-10**. Fig. 11 shows, once  
 628 again, that the chemical composition of emitted particles changes with their size because of a size-dependent  
 629 contribution from different sources of particle emission (*e.g.* fuel/oil combustion, unburnt oil).

### 630 3.4. Simulation results

631 Computational combustion modeling is an essential, complementary tool to engine experiments (Pitz  
 632 et al., 2007). Detailed soot models use extensive chemical mechanisms consisting of hundreds of chemical  
 633 reactions and detailed particle dynamics to predict the formation of soot particles. These kinds of models  
 634 are able to provide a deep insight into the soot formation and oxidation mechanism (Kong et al., 1995; Hong  
 635 et al., 2005; Pitz et al., 2007; Wu et al., 2019a,b). They provide the opportunity to efficiently optimize  
 636 the performance of internal combustion engines, allowing to represent the combustion of fuel in a variety of  
 637 practical devices (*e.g.* spark ignition direct injection engines). An essential component of such models is the  
 638 availability of extensive experimental data, for both fuel and combustion by-products, of sufficient quality to

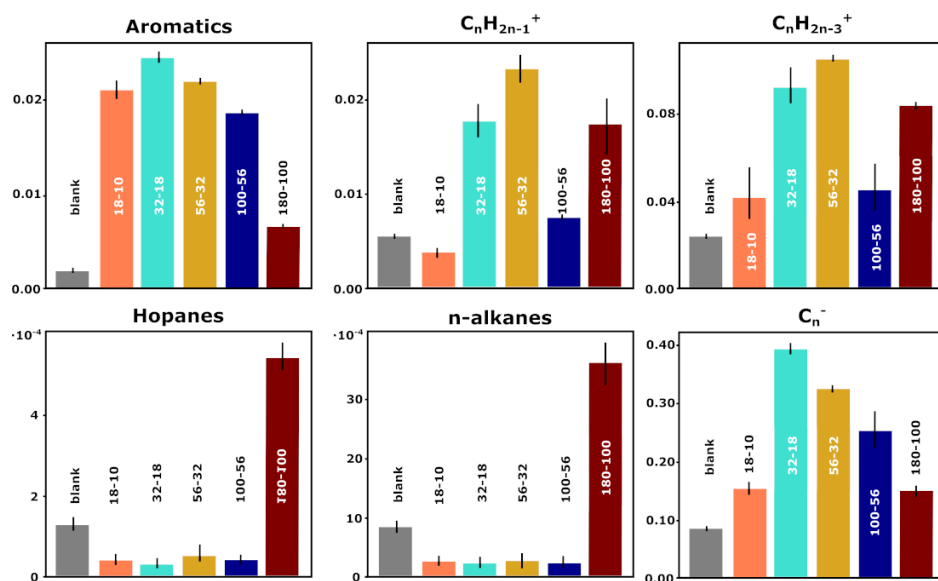


Figure 11: Integrated peak areas of positive and negative SIMS fragment ions of interest normalized to the total ion count (TIC) for particles produced in the **EM** engine regime (low air/fuel ratio). The error bars represent the standard deviation among all analyzed zones.

639 first identify important species that need to be included in the model and then validate it. The information  
 640 about the OC and EC content presented here was used to validate the model guided application (Lee et al.,  
 641 2019) utilized in the development and optimization of the particle number emission monitoring systems for  
 642 particulates down to 10 nm. Other findings (*e.g.* the size-dependent contribution of hopanoid species or  
 643 aliphatic compounds) can be subsequently used in the development of additional theoretical models, for  
 644 instance dedicated to assess the contribution of lubricating oil to particle emissions.

645 The SRM Engine Suite was first applied to model 12 steady state operating conditions of the gasoline  
 646 direct injection single-cylinder test engine. Experimentally obtained in-cylinder pressure profiles, gas phase  
 647 emissions (*e.g.* CO,  $\mu$ H<sub>C</sub>, NO<sub>x</sub>), particle concentrations and size distributions have been used to calibrate  
 648 the model. Additionally, size-resolved chemical composition was employed for its validation. Due to the  
 649 involved complexities, only one representative point is used here to compare with chemical characterization  
 650 results.

651 In-cylinder pressure profiles obtained experimentally showed good agreement with the outputs of the  
 652 model and hence ensure that the combustion behavior is modeled accurately, Fig. S12. **This is essential**  
 653 **because the particulate phase is directly coupled to the gas phase and detailed mechanisms are used for both**  
 654 **phases. In order to produce soot in the particulate phase, the necessary precursors need to be present in the**  
 655 **gas phase and this is only possible if the combustion characteristics are captured correctly.** A similar agree-  
 656 ment can be observed for the particle number (Fig. 12a) and size distributions, shown for several selected  
 657 operating points (Fig. 12b). In Fig 12, it can be observed that the simulated particle size distributions tend  
 658 to fit the larger size ranges poorly. This is acceptable as the experimental results also show larger errors for  
 659 the large particles. Besides that, this project is focused on the smaller particles around 10 nm, therefore  
 660 it is more important to simulate the formation of the smaller particles more accurately. It is also worth  
 661 mentioning that the particle size distributions have a peak around the 10 nm region and because of this,  
 662 the model calibration is weighted towards the smaller sizes. The peaks are not obvious in the plots because  
 663 the axes are logarithmically scaled.

664 The particle populations are then further used to calculate the SOF mass fraction and layer thickness  
 665 (Fig. 13) as well as the number of primary particles per aggregate and their size (Fig. S13). These results  
 666 allow for a comparison with experimental data obtained by off-line chemical characterization (*e.g.* organic  
 667 carbon content) and SEM measurements, respectively. **Fig. 13 demonstrates a sensitivity analysis of the**

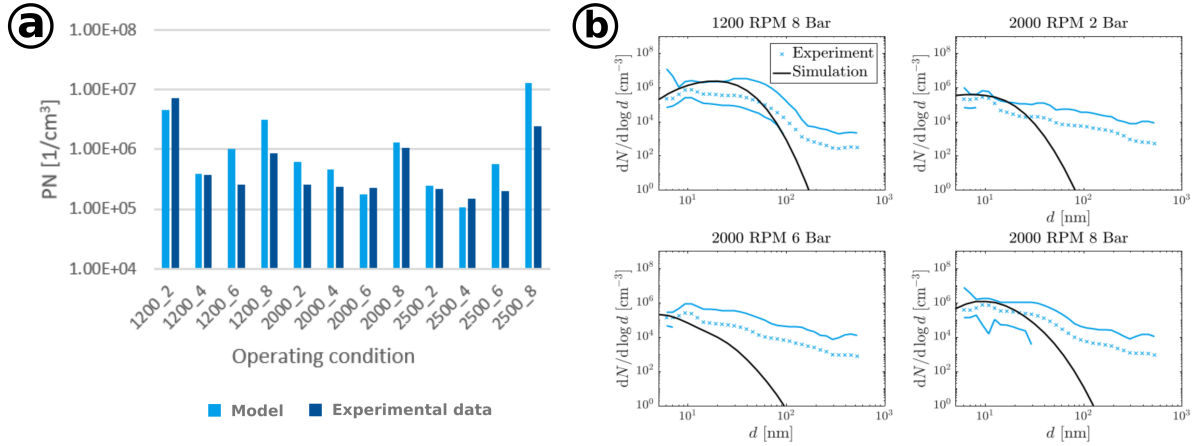


Figure 12: (a) – Calibrated PN for all studied operating points, (b) – Particle size distributions for a selection of operating points. The dashed lines represent the upper and lower bounds from the measurement data. Due to logarithmic scaling of the axes, some lower bounds with the value zero cannot be plotted.

668 effects of engine load on the formation of SOF on the particles. From the perspective of the chemical  
 669 characterization of the particles, the model is validated by comparing the SOF layer thickness with the  
 670 experimentally measured OC content (Section 3.3.4). The bump in the SOF layer thickness observed in the  
 671 measurements was mimicked well by the model. In this paper, only qualitative comparison is made between  
 672 the simulated and measured results from an operating point. The simulated results show that the quantity  
 673 of SOF is a strong function of the engine operating condition. Data from different operating conditions are  
 674 required to further validate and improve the model. The measurements and the model results also confirmed  
 675 that surface composition is not a measure of bulk characteristics. Based on the simulated results, the SOF  
 676 mass fraction shows a different trend compared to the SOF layer thickness. Lastly, the calculated primary  
 677 particle sizes as a function of aggregate size can be compared against results generated from SEM images  
 678 (e.g. Fig. 4) when more measurements become available in the future.

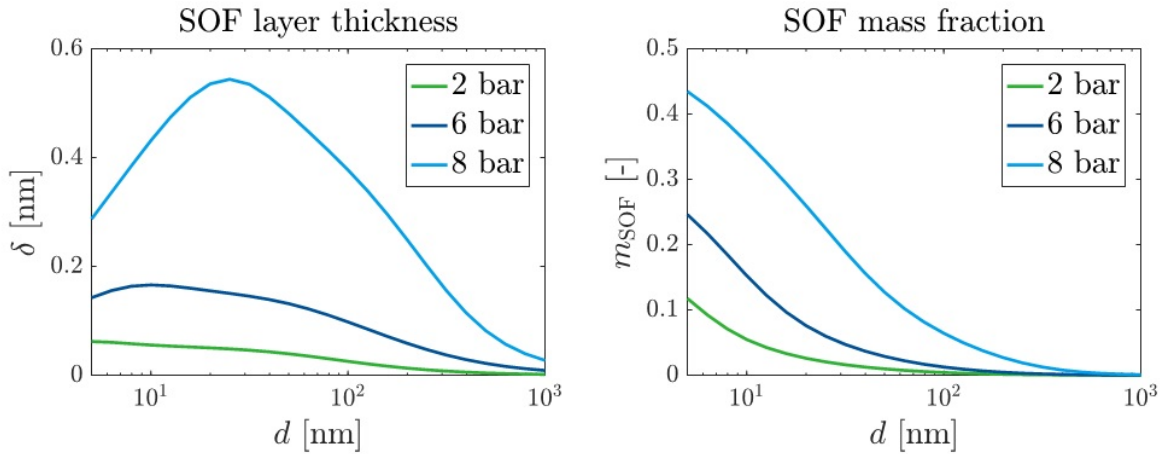


Figure 13: Sensitivity of SOF layer thickness and mass fraction with engine load. Engine speed is held constant at 2000 RPM.

## 679 Conclusions

680 Particles emitted by a gasoline single cylinder direct injection engine have been characterized by a  
 681 combination of on-line and off-line techniques enabling extensive information to be gathered relative to the

682 structure, morphology and composition of the particulate matter, and their variation with particle size.  
683 Detailed molecular-level characterization of size-selected particles by mass spectrometric techniques coupled  
684 with statistical procedures showed decisive evidence for the variation of the chemical composition with  
685 particle size. Moreover, identification of key chemical markers allowed clear discrimination of particles by  
686 source (fuel, lubricant, engine wear) and engine operating regime. It was also shown that a catalytic stripper  
687 that complies with European regulations for PMP systems (>99 % removal of  $\geq 30$  nm tetracontane)  
688 successfully removes the majority of particle-bound organic species. Atomic force and scanning electron  
689 microscopies were used to monitor the morphology of the collected particles, while Tip-Enhanced Raman  
690 Spectroscopy was used for the first time to probe the nanostructure of sub-10nm combustion-generated  
691 particles. The latter showed that ultrafine particles that are produced and collected in the same engine  
692 regime can be still very different.

693 Model Guided Application comprising physico-chemical simulation and advanced statistics has been  
694 formulated as part of the development of PEMS methodology to support the understanding of the formation  
695 and evolution of the particles in the engine up to the measurement sampling line. The results demonstrate  
696 the ability to use a model-based framework to assess the performance of an experimental setup. The  
697 particle measurements ranging from particle number concentrations, particle size distributions and chemical  
698 composition are essential to calibrate and validate the detailed physico-chemical model presented in this  
699 paper. It is important to note that such measurement data is highly relevant for improving the fidelity of  
700 a variety of modeling approaches, ranging from 0D, 1D engine cycle, to 3D computational fluid dynamics,  
701 particularly, given the poor predictive capability of simulation tools for particulate emissions. The modeling  
702 work presented in this paper is related to a single-cylinder test engine, and is also directly applicable to  
703 multi-cylinder engines as well as at vehicle level.

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707 **References**

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