

Time-resolved characterization of primary particle emissions and secondary particle formation from a modern gasoline passenger car

P. Karjalainen¹, H. Timonen², E. Saukko¹, H. Kuuluvainen¹, S. Saarikoski², P. Aakko-Saksa³, T. Murtonen³, M. Bloss², M. Dal Maso¹, E. Ahlberg^{4,5}, B. Svenningsson⁵, W.H. Brune⁶, R. Hillamo², J. Keskinen¹ and T. Rönkkö¹

[1]{Aerosol Physics Laboratory, Department of Physics, Tampere University of Technology, P.O. Box 692, FIN-33101 Tampere, Finland}

[2]{Atmospheric Composition Research, Finnish Meteorological Institute, P.O. Box 503, 00101, Helsinki, Finland}

[3]{VTT Technical Research Centre of Finland Ltd., P.O. Box 1000, 02044 VTT, Espoo, Finland}

[4]{Centre for Environmental and Climate research, Lund University, Box 118, SE-22100 Lund, Sweden}

[5]{Division of Nuclear Physics, Lund University, Box 118, SE-221 00 Lund, Sweden}

[6]{Department of Meteorology, Pennsylvania State University, University Park, PA, USA}

Correspondence to: T. Rönkkö (topi.ronkko@tut.fi)

Abstract

Changes in vehicle emission reduction technologies significantly affect traffic-related emissions in urban areas. In many densely populated areas the amount of traffic is increasing, keeping the emission level high or even increasing. To understand the health effects of traffic related emissions, both primary (direct) particulate emission and secondary particle formation (from gaseous precursors in the exhaust emissions) need to be characterized. In this study we used a comprehensive set of measurements to characterize both primary and secondary particulate emissions of a Euro 5 level gasoline passenger car. Our aerosol particle study

1 covers the whole process chain in emission formation, from the tailpipe to the atmosphere,
2 and takes into account also differences in driving patterns. We observed that in mass terms,
3 the amount of secondary particles was 13 times higher than the amount of primary particles.
4 The formation, composition, number, and mass of secondary particles was significantly
5 affected by driving patterns and engine conditions. The highest gaseous and particulate
6 emissions were observed at the beginning of the test cycle when the performance of the
7 engine and the catalyst was below optimal. The key parameter for secondary particle
8 formation was the amount of gaseous hydrocarbons in primary emissions; however, also the
9 primary particle population had an influence.

10

11 **1 Introduction**

12 Vehicular emissions deteriorate the air quality locally (Wehner et al., 2002; Pirjola et al.,
13 2012; Lähde et al., 2014) and contribute significantly to the air pollution levels in urban areas.
14 Air pollution components like particulate matter contribute to adverse health effects of people
15 (e.g. Pope III and Dockery, 2006). The human exposure to pollutants in urban environments is
16 the highest in the vicinity of traffic. In order to reduce the adverse health effects and exposure
17 of people by pollutants, the emission regulation for vehicles with direct injection engines
18 include limits for particulate mass (PM), and in Europe for some vehicle types, particle
19 number (PN) (Dieselnet), of which the PN limit is considered to be stricter. Limits for
20 gaseous compounds cover total hydrocarbon emissions, nitrogen oxides and carbon
21 monoxide. Both particulate and gaseous emissions are strongly affected by technology
22 development (e.g. catalysts and filters), driven by legislation activities. This technology
23 development has, in general also other effects than required by emission legislation, for
24 example fuel sulphur content limitations affect the emissions of nanoparticles. It should be
25 noted that e.g. semi-volatile compounds (e.g. low-volatility organics, sulphuric compounds)
26 are not directly regulated even though they are partially detected in the gravimetric PM
27 determination as particles or adsorbed gas phase artefacts (Chase et al., 2004; Högström et al.,
28 2012). Although not directly regulated, low-volatility organics are likely to be affected by
29 gaseous hydrocarbons limits.

30 In the gasoline vehicle fleet the port-fuel injection (PFI) techniques has been widely replaced
31 by gasoline direct injection (GDI) technologies due to the need to decrease fuel consumption
32 and NO_x emissions of passenger cars (e.g. Alkidas, 2007; CARB, 2010). The disadvantage of

1 GDI technologies is the increased primary particle emission (Aakko and Nylund, 2003; Mohr
2 et al., 2006; Braisher et al., 2010). The GDI vehicle exhaust particle number concentrations
3 are typically significantly lower than the diesel exhaust particle concentrations without a
4 diesel particulate filter (DPF) but higher than concentrations with a DPF (Mathis et al., 2005).
5 The GDI engine exhaust particle size distribution has been observed to be bi-modal (Barone
6 et al., 2012; Sementa et al., 2012; Sgro et al., 2012; Maricq et al., 1999; Karjalainen et al.,
7 2014; Pirjola et al., 2015a) and the emission is dominated by elemental carbon (EC) (Maricq
8 et al., 2012). Organic carbon (OC) constitutes only a small fraction of particle emissions.
9 Particles are (in number) mainly in ultrafine particle sizes (e.g. Maricq et al., 1999; Harris and
10 Maricq, 2001; Khalek et al., 2010; Karjalainen et al., 2014). According to the study of
11 Karjalainen et al. (2014), the GDI exhaust particles can be divided into four different types:
12 spherical amorphous particles consisting of carbon with mean particle size between 10 and 20
13 nm (see also Sgro et al., 2012; Barone et al., 2012), agglomerated soot like particles with
14 mean particle size between 30 and 60 nm, lubricant oil originating particles consisting of
15 metallic ash components (Rönkkö et al., 2014) and semivolatile nucleation particles (see also
16 Mathis et al., 2005; Li et al., 2013). The highest emissions of primary particles take place
17 under acceleration and deceleration conditions (Karjalainen et al., 2014).

18 Secondary aerosol formation happens in the atmosphere through oxidation processes that tend
19 to lower the saturation vapor pressures of organic species. Thus, more oxidized compounds,
20 mostly organic compounds, are more likely found in the particle phase (Robinson et al.,
21 2007). Fresh exhaust emissions contain a variety of different organic compounds, in the scale
22 of hundreds or thousands of different components (Rogge et al., 1993). Part of those has low
23 saturation vapour pressure already when emitted and thus they are observed in primary
24 particulate emission or in particulate phase after the exhaust has been diluted rapidly into the
25 atmospheric conditions (Tobias et al., 2001; Sakurai et al., 2003; Arnold et al., 2012; Pirjola
26 et al., 2015b). However, even the majority of organic compounds in the exhaust are primarily
27 emitted to atmosphere in gaseous phase. Also, sulphur compounds such as SO₂ as well as
28 nitrogen oxides can play a role in the secondary aerosol formation processes in the
29 atmosphere.

30 There are studies of engine exhaust related secondary organic aerosol (SOA) formation for
31 gasoline (Suarez-Bertoa et al., 2015; Nordin et al., 2013; Platt et al., 2013; Gordon et al.,
32 2014) and diesel vehicles (e.g. Weitkamp et al., 2007; Chirico et al., 2010; Gordon et al.,

1 2013). In these, the secondary particulate emissions of gasoline vehicles have been studied
2 using a smog chamber so that diluted exhaust gas has been led to the smog chamber during a
3 test cycle, a constant speed operation or idling condition (Chirico et al., 2010; Nordin et al.,
4 2013). However, in the emission's perspective this represents only the average over the test,
5 and more detailed analysis of the effect of driving pattern and engine conditions on SOA
6 formation is lacking. With the potential aerosol mass (PAM) concept (Kang et al., 2007,
7 2011) SOA emissions can be studied in a shorter time scale (minutes). The PAM is a flow-
8 through type reactor that uses UV lamps to form oxidants (O_3 , OH, HO_2). Secondary aerosol
9 formation processes are accelerated so that few minute residence time corresponds the
10 atmospheric ageing of several days or even weeks. In principle, the PAM reactor enables real-
11 time measurements of secondary particulate emissions during the driving cycle. The PAM
12 concept has been previously applied in vehicular exhaust studies e.g. by Tkacik et al. (2014)
13 who used the reactor in a traffic tunnel to study the secondary aerosol properties, and by
14 Pourkhesalian et al. (2015) who used the PAM reactor in connection with diesel exhaust
15 particle volatility and Reactive Oxygen Species (ROS) studies. High oxidant concentrations,
16 (100–1000 times atmospheric concentrations of O_3 , OH, HO_2) and UV lights used in the
17 chamber are shown to simulate SOA formation in the atmosphere (Kang et al., 2007; Kang et
18 al., 2011). The aging as the sample flows through the chamber is shown to represent several
19 day aging in the atmosphere (Kang et al., 2011; Ortega et al., 2013).

20 In this work the aim is to show how the driving conditions of modern gasoline vehicle affect
21 the emissions, especially the secondary particulate emission. To meet this goal,
22 comprehensive set of real-time instruments was used to study the physical and chemical
23 characteristics of primary and secondary particle emissions as well as gaseous emissions of a
24 modern GDI passenger car. The sampling of exhaust for primary emission measurements was
25 conducted by mimicking the real-world atmospheric dilution. Secondary emission was
26 studied by using a PAM reactor designed to mimic atmospheric ageing of aerosol.
27 Experiments were performed for the official European test cycle for passenger cars that is the
28 New European Driving Cycle (NEDC). Special attention was paid to the temporal behavior of
29 primary and secondary particle emissions, e.g. emissions during the engine cold start and in
30 different driving patterns.

1 **2 Materials and methods**

2 The test vehicle was a modern gasoline passenger car (model year 2011, 1.4 l turbo-charged
3 GDI engine, 7 gear dual clutch automatic transmission, weight 1557 kg, odometer reading 48
4 700 km, emission level Euro 5 with a three-way catalytic converter). Test fuels comprised of
5 regular commercial E10 (max 10% ethanol) with sulphur content being below 10 ppm. The
6 driving cycle used in the study was New European Driving Cycle (NEDC) (Figure 2a). The
7 European exhaust emissions driving cycle “NEDC” is defined in the UN ECE R83 regulation.
8 The car was tested on a chassis dynamometer in a climatic test cell at +23 °C. NEDC totals
9 11.0 km, here divided into three test phases to study emissions at cold start and with warmed-
10 up engines. The first and second test phases (later called as cold start urban driving cycle,
11 CSUDC, and hot urban driving cycle, HUDC) each consisted of 2.026 km driving, and the
12 third test phase, the extra-urban driving cycle (EUDC), was 6.955 km.

13 As shown in Fig. 1, particle sampling was conveyed by a partial exhaust sampling system
14 (Ntziachristos et al., 2004) at thermally insulated and externally heated exhaust transfer line
15 (material Stainless steel AISI 316L). The sampling system consisted of a porous tube diluter
16 (PTD) (dilution ratio (DR) 12, dilution nitrogen temperature 30 °C), residence time chamber
17 (2.5 s) and secondary dilution conducted by Dekati Diluter (DR 8). In terms of exhaust
18 nucleation particle formation, the sampling system mimics the real exhaust dilution and
19 nanoparticle formation processes in atmosphere (Rönkkö et al., 2006; Keskinen and Rönkkö,
20 2010).

21 A potential aerosol mass (PAM) chamber is a small flow through chamber developed to
22 simulate aerosol aging in the atmosphere. The PAM chamber was installed between the
23 ageing chamber and secondary dilution units of sampling system. PAM chamber is
24 thoroughly described by Kang et al., (2007, 2011) and Lambe et al., (2011, 2015). Shortly,
25 PAM chamber is a stainless steel cylinder (length 46 cm, diameter 22 cm, volume ~13 l). In
26 an effort to reduce wall effects the PAM flow reactor was designed with a larger radial/axial
27 dimension ratio and a smaller surface to volume ratio relative to other flow reactors (Lambe et
28 al., 2011, Kang et al., 2011). Two UV-lamps (BHK Ink., Ca) were used to produce oxidants
29 (O_3 , OH and HO_2) as well as UV-light (185 nm, 254 nm). The sample flow through the PAM
30 chamber was set to ~9.75 l/min resulting average residence time of 84 s. Voltage of the two
31 UV lamps was at maximum value, 190 V. Relative humidity (RH) and temperature were
32 measured prior to the PAM with stable values of 60% and 22 °C, respectively. Typically

1 ozone concentration after the PAM was on average 6 ppm. The PAM chamber was calibrated
2 using average experiment conditions and following the same procedure described by Lambe
3 et al. (2011). The corresponding OH exposure was calculated to be 1.03E+12, representing
4 approximately 8 days of aging in the atmosphere.

5 PAM chamber has been used in different ambient environments (Palm et al., 2015; Ortega et
6 al., 2015; Tkazik et al., 2013) and also thoroughly characterized in the laboratory conditions
7 via measurements and modelling (e.g. Lambe et al., 2011, 2015; Peng et al., 2015; Ortega et
8 al., 2013). The Oxidant concentrations in the PAM chamber are higher (100-1000 times) than
9 in atmosphere (Kang et al., 2007), however the ratios between oxidants are similar to
10 atmosphere. Several studies (e.g. Kang et al., 2007, 2011) have compared PAM results to
11 atmospheric results. Kang et al. (2007, 2011) showed that the yields of OA from individual
12 organic precursor gases were similar to those obtained in large environmental chambers and
13 that the extent of OA oxidation appears to be similar to that observed in the atmosphere and
14 greater than that observed in large environmental chambers and laboratory flow tubes. Also,
15 according to results of Tkazik et al., (2013) the chemical evolution of the organic aerosol in
16 the PAM reactor is similar to that observed in the atmospheric measurements. Also, Tkazik et
17 al., (2013) observed that the mass spectrum of the unoxidized primary organic aerosol closely
18 resembles ambient hydrocarbon-like organic aerosol (HOA) and that aged PM firstly
19 resembles semivolatile oxygenated organic aerosol (SV-OOA) and then low-volatility organic
20 aerosol (LV-OOA) at higher OH exposures. In this study, cycles were firstly run without the
21 PAM chamber to measure primary emissions and secondly with the PAM chamber in order to
22 study the formation of secondary particulate material. Before the experiment, the PAM
23 chamber was cleaned by running pure N₂-O₂ mixture with UV-lights on.

24 Transmission efficiency of gases (CO and SO₂) in PAM chamber has shown that wall losses
25 in the PAM chamber are very small (Lambe et al., 2011). Primary particle losses for a PAM
26 chamber (results shown in Fig. S1) are in general small especially in the particle sizes that
27 contain most of the aerosol mass: 25% at 50 nm, 15% at 100 nm and below 10% above 150
28 nm.

29 The particle instrumentation was located downstream of the secondary diluter. The particle
30 size distributions were measured on-line (1 Hz time resolution) with a High-resolution low-
31 pressure impactor (HRLPI) (Arffman et al., 2014)), fitted into an ELPI bodywork to replace
32 the original charger and impactor, and an Engine exhaust particle sizer (EEPS, TSI Inc.)

1 (Johnson et al., 2004). The particle number concentration was also measured with an ultrafine
2 condensation particle counter (UCPC, TSI Inc. model 3025) that was located downstream of a
3 passive nanoparticle diluter (DR 42). A SP-AMS was used to measure chemical composition
4 (ions, organic carbon, refractory black carbon and some metals) of emitted submicron (50–
5 800 nm) particulate matter (PM). SP-AMS is a high resolution time-of-flight aerosol mass
6 spectrometer (HR-ToF-AMS) with added laser (intracavity Nd:YAG, 1064 nm) vaporizer
7 (Schwarz et al., 2008). The HR-ToF-AMS is described in detail by (DeCarlo et al., 2006;
8 Jayne et al., 2000) and SP-AMS is described by (Onasch et al., 2012; Schwarz et al., 2008).
9 Briefly, in the SP-AMS an aerodynamic lens is used to form a narrow beam of particles that is
10 transmitted into the detection chamber, where the species are flash-vaporized. Particles are
11 vaporized either by normal tungsten vaporizer at 600 °C to analyze inorganic ion and OC
12 concentrations or with SP laser (intracavity Nd:YAG, 1064 nm) in order to analyze black
13 carbon and metals. The vaporized compounds are ionized using electron impact ionization (70
14 eV). Ions formed are guided to the time-of-flight chamber. A multi-channel plate (MCP) is
15 used as a detector. The time resolution of AMS measurements was five seconds. One-minute
16 detection limits for submicrometer particles are $< 0.04 \mu\text{g m}^{-3}$ for all species in the V-mode.
17 The IGOR 6.11 (Wavemetrics, Lake Oswego, OR), Squirrel 1.53 (Sueper, 2013) and PIKA
18 1.12F were used to analyze the SP-AMS data. Elemental analysis (based on Aiken et al.,
19 2008) was performed on the HR-ToF-AMS data to determine the aerosol hydrogen-to-carbon
20 (H/C) and oxygen-to-carbon (O/C) ratios. CO₂ concentrations during the measurement period
21 were significantly higher (up to 1450 ppm) than atmospheric values (400 ppm), thus CO₂
22 time-series was used to correct the artefact caused by gaseous CO₂. Collection efficiency (CE)
23 of 1 was used in this study. We note that chosen CE has no effect on calculated ratios.

24 Equipment used in the measurement of the CO, HC, and NO_x emissions conforms to the
25 specifications of the Directive 70/220/EEC and its amendments. The true oxygen contents and
26 densities of the fuels were used in the calculation of the results. A flame ionization detector
27 (FID) was used for the measurement of hydrocarbons (all carbon-containing compounds, also
28 oxygenates) (Sandström-Dahl et al., 2010; Aakko-Saksa et al., 2014). The calculation method
29 chosen uses the density of 619 kg m^{-3} (different from the EC regulation 692/2008). A number
30 of gaseous compounds (19 in total), amongst others nitrogen dioxide (NO₂), ammonia (NH₃),
31 nitrous oxide (N₂O), ethanol, formaldehyde and acetaldehyde were measured on-line with
32 two-second time resolution using Fourier transformation infrared (FTIR) equipment (Gasmeter
33 Cr-2000).

1 **3 Results and discussion**

2 **3.1 Primary particulate and gaseous emissions of gasoline passenger car**

3 **3.1.1 Particle size distributions**

4 The driving cycle used in the study was NEDC being a statutory cycle in emission testing in
5 Europe. The cycle consists of several patterns describing typical driving in urban
6 environments and high-way driving (Fig. 2a) with total duration and length of the cycle is
7 1200 s and 11.0 km, respectively. Fig. 2 shows the speed of the test vehicle during the test
8 cycle and particle number concentration, particle volume concentration and particle size
9 distribution of vehicle exhaust, all measured with high time resolution (1 s).

10 The exhaust particle number concentration was strongly dependent on driving condition (Fig.
11 1b). Large particle number concentrations were observed during accelerations, especially
12 during the first two accelerations when the engine had not yet reached steady temperature
13 conditions, and they were therefore associated with high engine loading and altering
14 combustion conditions. In addition to soot particles (particle diameters of 30–100 nm, see Fig.
15 1c), there were also frequent observations of small particles ($D_p < 10$ nm), especially in the
16 middle part of the cycle. These nanoparticles are most likely associated with deceleration and
17 engine braking conditions (Rönkkö et al., 2014; Karjalainen et al., 2014). The largest particle
18 volume concentrations were observed at the beginning, just after ignition and, on the other
19 hand, at the end of the test cycle when the driving was at high speed and engine load. High
20 total particle volume concentrations were strongly linked with the existence of soot mode
21 particles in the exhaust.

22 **3.1.2 Chemical composition**

23 Fig. 3 shows the chemical composition of primary exhaust particles during the NEDC cycle.
24 The lower pane shows the major components, revealing that the large particle emission at the
25 beginning of the cycle consists mainly of organic compounds and refractory black carbon
26 (rBC). When compared to Fig. 2, it can be seen that the organic compounds together with rBC
27 forms the so called soot mode, which dominate the particle volume concentration due to its
28 large particle size. While the rBC has formed in the engine due to the incomplete combustion
29 of fuel forming agglomerated soot particles (Heywood, 1988), the organic compounds have
30 likely been condensed onto the soot particle surface mainly during cooling dilution process of

1 exhaust. Fig. 3 shows that later, after the starting phase of the test cycle the relative
2 concentration of rBC decreases and remains at low levels with the exception of the
3 accelerations at the highway part of the cycle. Interestingly, the concentration of organic
4 compounds was very significant in the middle part of the cycle, i.e. when the emissions of
5 nanoparticles (see Fig. 2) were observed to be high. Thus, while the high emission of organic
6 compounds seems to be linked with high soot/rBC emission at the beginning of the cycle, in
7 the middle part the organics and rBC emissions seemed not to be interlinked.

8 Concentrations of inorganic species (SO_4 , NH_4 , NO_3 , Cl) are shown in the upper pane of Fig.
9 3. Note that the concentration axes differ. In general, the highest sulphate and nitrate
10 concentrations existed during accelerations, and had a good correlation with soot/rBC
11 emissions. The sulphate concentration increases also during certain periods in the middle part
12 of the cycle, clearly linked with similar peaks in organic compounds concentration (see Fig.
13 3). Interestingly, during highway driving and the following deceleration, also significant
14 concentration of ammonium, nitrate and chloride ions were observed.

15 **3.1.3 Gaseous emissions**

16 The time series of total hydrocarbons, ammonia and NO_x during the NEDC test cycle are
17 presented in Fig. 4. The largest hydrocarbon emissions were observed at beginning of the
18 cycle due to low engine and exhaust gas temperatures, which lowers the efficiency of the
19 oxidation process in the three-way catalytic converter, in addition to higher formation rates of
20 gaseous hydrocarbons during combustion. The hydrocarbon emissions are in line with the
21 measurements of the chemical composition of particles, which shows that the highest
22 emissions of particulate organic compounds occur at the beginning of the cycle. However,
23 during the middle part of the cycle the emissions of gaseous hydrocarbons and organic
24 particulate matter did not correlate; although in particle phase organics (see Fig. 3) the
25 concentrations reached high values also during middle part of the cycle, the gaseous
26 hydrocarbons remained at very low level until to the highway driving part of the cycle. The
27 NO_x emissions were the highest at the beginning of the cycle and during the last part of the
28 cycle when the driving speed and combustion temperatures were high. Ammonia
29 concentrations were at the level of 10 ppm during most of the cycle, even higher than 100
30 ppm concentration was measured during the accelerations at the end of the cycle. The highest
31 ammonia concentrations were clearly linked with acceleration, under conditions when the air-
32 to-fuel ratio can be below 1 (rich mixture). This is in line with the findings by Meija-Centeno

1 et al. (2007) and Heeb et al. (2006) showing ammonia formation in the three-way catalyst in
2 slightly rich air-to-fuel ratios, which are prevailing during acceleration.

3 **3.2 Secondary particle formation from a gasoline passenger car**

4 **3.2.1 Particle size distributions**

5 Fig. 4 shows the secondary particle number concentrations, volume concentrations and size
6 distributions of gasoline passenger car exhaust during the NEDC cycle. In general, the
7 volume and number concentrations as well as mean particle size of secondary particles were
8 significantly larger than those of the primary particles, throughout the cycle. Periodic
9 behaviour similar to that of the primary particles can be observed: first a period with large
10 soot mode particles, then a period with a large number of small nanoparticles, and finally the
11 highway part of the cycle.

12 As shown above, after the ignition the emissions of gaseous precursors (hydrocarbons and
13 nitrogen containing species) and primary particles were observed to be high (Fig. 4). This
14 combined with the information seen in Fig. 5 indicates that the existence of gaseous
15 precursors in the exhaust significantly increases the secondary particulate matter formation,
16 resulting as a high volume concentration of large particles at the beginning of the test cycle
17 (Fig. 5). Compared to other periods of the cycle, at the beginning the volume concentration of
18 secondary particles was three times higher, highlighting the role of cold starts in total
19 secondary particle emission of gasoline vehicles.

20 The high oxidant concentrations in the PAM chamber result also in high concentrations of
21 condensing compounds, which causes a possibility for nucleation in the chamber. In this
22 study we measured higher particle number concentrations for the sample treated by the PAM
23 than for the untreated sample. However, the increase of particle number was not very
24 significant and, in principle, may also be caused by the increase of particle size into the
25 measurement range on aerosol instruments. Interestingly, nanoparticles were not observed in
26 the primary emission during the first period of cycle (Fig. 2), when both the precursor gas
27 concentration and resulted volume of secondary particulate matter was the highest. During the
28 first period, also the mean particle number concentrations were on a relatively similar level
29 both in the primary and secondary aerosol. Instead, nanoparticles were observed in the sample
30 treated by the PAM during the second phase (starting at 400 s) of the cycle. During this part
31 of the test cycle the nanoparticles existed also in primary emissions. Thus the results indicate

1 that nanoparticles found after PAM chamber are obviously initially formed already before the
2 sample was introduced into the PAM chamber. It should be kept in mind that the existence
3 and growth of nanoparticles in the PAM chamber can slightly change the mean particle size
4 and thus how effectively they are detected by aerosol instruments; e.g. the particle size range
5 of aerosol mass spectrometers do not typically cover particles smaller than 50 nm, and in
6 several studies the particle number size distribution measurement is limited to sizes above 10
7 nm.

8 As stated above, in the middle part of the cycle, a large number of primary nanoparticles was
9 introduced into the chamber from the exhaust. Fig. 4 shows that these sub-5 nm particles grew
10 in the chamber to particle sizes similar to primary soot particles. This takes approximately
11 60–80 s, corresponding to the mean residence time in the PAM. In general, it seems that both
12 the primary soot particles and primary nanoparticles can have an important role in secondary
13 particle formation dynamics resulting e.g. in the size distribution of aged exhaust aerosol.

14 **3.2.2 Chemical composition of secondary particles**

15 The secondary aerosol mass consisted mainly of organic compounds and rBC (Fig. 6, lower
16 pane). At the beginning of the test cycle, the concentrations of organic compounds in the
17 secondary particulate matter were about 100 times higher than their concentrations in primary
18 particles, while the O:C ratio dipped below 0.5 (see Fig. S3). During other parts of the cycle
19 the concentrations of the organic compounds were significantly lower and remained relatively
20 stable. The rBC concentration level did not change significantly because rBC is a primary
21 component.

22 At the beginning of the cycle the incomplete combustion causes high emissions of rBC and
23 gaseous hydrocarbons. Simultaneously the temperature of the three-way catalyst is low and
24 thus the reduction of hydrocarbons is not optimal. In the PAM reactor, the oxidation of
25 hydrocarbons lowers their volatility which results in high emissions of secondary particulate
26 matter consisting of organic compounds. During highway part of the cycle, the incomplete
27 combustion again causes the emission of soot/rBC during certain acceleration phases.
28 However, during highway part the temperature of the catalyst used in the vehicle is very high,
29 approximately 700 °C (see Karjalainen et al., 2014), meaning that it keeps the emissions of
30 gaseous hydrocarbon emissions at a very low level. Thus, during the highway part the
31 concentration of organic precursors is low in the exhaust, resulting in a low concentration of
32 secondary organic particulate material.

1 In addition to rBC and organic compounds, during the middle part of the cycle the
2 concentrations of inorganic species were observed to be stable. Only a slight increase in
3 sulphate concentration was observed, simultaneously with the existence of nanoparticles in
4 secondary aerosol. This observation is in line with primary particle measurements where
5 sulphate peaks were observed during the middle part of the cycle. During the highway part of
6 the cycle the concentrations of inorganic species in the secondary particulate matter increases
7 when compared to the previous parts of the cycle. This is seemingly caused by high emissions
8 of gaseous nitrogen compounds (see Fig. 4). Results indicate that also these compounds may
9 have a significant role in traffic related secondary aerosol formation. However, this kind of
10 aerosol is very specifically formed only at high vehicle speeds.

11 **3.2.3 Influence of driving conditions to emission characteristics**

12 The results presented above indicate that both the primary and secondary emissions vary
13 strongly as a function of the driving cycle. To clarify the effects of driving conditions on the
14 concentrations of secondary and primary particles the cycle was divided into three sections
15 according to the engine and speed profile conditions: CSUDC (0–391 s), HUDC (392–787 s)
16 and EUDC (788–1180 s). The CSUDC represents cold start situation, the HUDC represents
17 typical city driving with warm engine and the EUDC represents typical highway driving. Fig.
18 7 shows chemical composition and O:C –ratios of primary and secondary (primary
19 components excluded) exhaust particles for these three sections. O:C –ratios were determined
20 for organic compounds based on chemical composition measured by the SP-AMS, so that
21 inorganic species and rBC were excluded. Emission factors for measured compounds are
22 presented in the Supplementary material (see Fig. S4 and Table S1).

23 Primary particle emissions were dominated by rBC and organics. It should be noted that
24 although the CSUDC and HUDC were similar from the viewpoint of driving conditions, the
25 rBC concentration was four times higher during CSUDC. Again, during the EUDC section of
26 the cycle higher rBC concentration was observed in the exhaust. In contrast, for the organics
27 similar differences between the sections of the test cycle were not observed. Inorganic
28 species concentrations were relatively low in all cycle sections representing on average 3.6%
29 of particulate mass.

30 On average, the secondary particulate emissions were 13 times higher than the primary
31 particle emissions. This value is higher or at similar level than observed in previous studies
32 reported. For instance, Suarez-Bertoa et al. (2015) reported 2–4 times higher values for the

1 secondary particle emissions of gasoline vehicle when compared to the primary organics and
2 BC. In the diesel exhaust study of Chirico et al. (2010), the secondary and primary particle
3 emissions were at similar level. However, in the study of Platt et al. (2013) SOA emission
4 was around 14 times higher than primary organic aerosol (POA) emission when they
5 measured the emissions of gasoline vehicle for the NEDC cycle. All of these studies were
6 conducted using a batch chamber while in our study a flow through chamber was used. The
7 differences between the studies can be due to the differences in the emissions but also due to
8 the differences in wall losses, exhaust and oxidant concentrations, and photochemical ages.

9 The chemical composition of secondary particles differed significantly from primary
10 particles; in secondary particles most of the particulate matter consisted of organics, in
11 primary particles the role of rBC was significant. The calculated secondary organics
12 concentration was high especially during CSUDC, even 9.9 mg m^{-3} . This highlights the
13 important role of primary and secondary emissions followed by the cold start. It should be
14 noted that the emission factors of both primary and secondary particles were lowest during the
15 EUDC (see Supplementary material).

16 O:C –ratios were relatively stable for primary emissions, slightly higher O:C –ratio (0.27) was
17 observed for the CSUDC. Similar O:C –ratios have been typically observed for fresh traffic
18 emissions in urban ambient measurements (Timonen et al., 2013; Carbone et al., 2014). For
19 the secondary emissions the O:C –ratios were between 0.5–0.6. Large hydrocarbon emissions
20 and probably differences in oxidation levels of primary gaseous compounds at the beginning
21 of the cycle likely affect, as well as, differences in oxidant levels in chamber are likely
22 reasons for observed differences. Previous studies for gasoline vehicle reported high O:C –
23 ratios (up to 0.7) for secondary organic exhaust aerosol (Suarez-Bertoa et al., 2015; Platt et
24 al., 2013) but also lower ratios of ~ 0.4 (Nordin et al., 2013).

25 **4 Conclusions**

26 In this study we characterized primary particle and gaseous emissions and secondary particle
27 formation from a Euro 5 emission level direct injection gasoline vehicle. All the
28 measurements were made in real time with high time resolution. Measurements were
29 conducted under driving conditions representing typical urban driving cycles. Our aim was to
30 create a basis for understanding the links between driving conditions, primary emissions of
31 aerosols and their precursors and the formation of secondary particulate material. We
32 approached this issue by using a potential aerosol mass (PAM) chamber enabling the

1 characterization of secondary emissions in real time, combined with comprehensive
2 characterization of PM and gaseous compounds.

3 Our results indicated higher or similar level secondary particulate matter emissions compared
4 to the previous studies (Suarez-Bertoa et al., 2015; Platt et al., 2013). Compared to primary
5 particle emissions, our study indicated 13 times higher secondary particulate emissions,
6 dominated by organics. The study of Suarez-Bertoa et al. (2015) indicated 2–4 times higher
7 emissions for secondary particles, instead, in the study of Platt et al. (2013) SOA emission
8 was around 9–15 times higher than POA emission for the NEDC cycle. For reference, the
9 primary particle emissions measured in this study were at similar levels than in previous
10 studies for modern gasoline vehicles (Karjalainen et al., 2014).

11 We observed that during ignition and during the first few minutes of the test cycle, i.e. when
12 the engine and the catalyst had not reached normal operation temperatures, the emissions of
13 primary PM and precursor gases were the largest and therefore a large amount of secondary
14 organic emission was formed. The following similar driving cycle with a warmed engine
15 produced significantly lower primary and secondary particulate emissions. This indicates that
16 the adverse effects of traffic are likely to be largest in city areas where driving distances are
17 typically short, near houses and workplaces. However, we note that the formation of
18 secondary particulate matter is a longer-time atmospheric process and thus not directly linked
19 with human exposure and human health at the site of emission. Also, it is reasonable to
20 assume that this problem at least from the viewpoint of secondary aerosol precursor emissions
21 is magnified under cold climatic conditions.

22 Both primary and secondary emissions were highly dependent on driving conditions, such as
23 speed, acceleration and deceleration profiles. At high speed (EUDC), both particulate mass
24 and size distribution were different when compared to low speed driving (HUCD). In
25 addition, under deceleration conditions very small nanoparticles were observed in primary
26 exhaust. These nanoparticles grew in particle size due to the condensation of highly oxidized
27 engine origin compounds; these oxidized compounds were formed in our experiment in the
28 PAM chamber but when forming in the atmosphere likely exhibits similar behaviour and
29 prefer to condense on the nanoparticles. Thus, our results indicate that also nanoparticles can
30 contribute to atmospheric secondary aerosol formation, especially on size distribution of
31 secondary particles. Due to that it is clear that current legislation focusing on larger particles
32 (PM mass or number of particles larger than 23 nm in diameter) is not optimal from the

1 viewpoint of realistic urban air quality, since it takes into account only the largest primary
2 particles.

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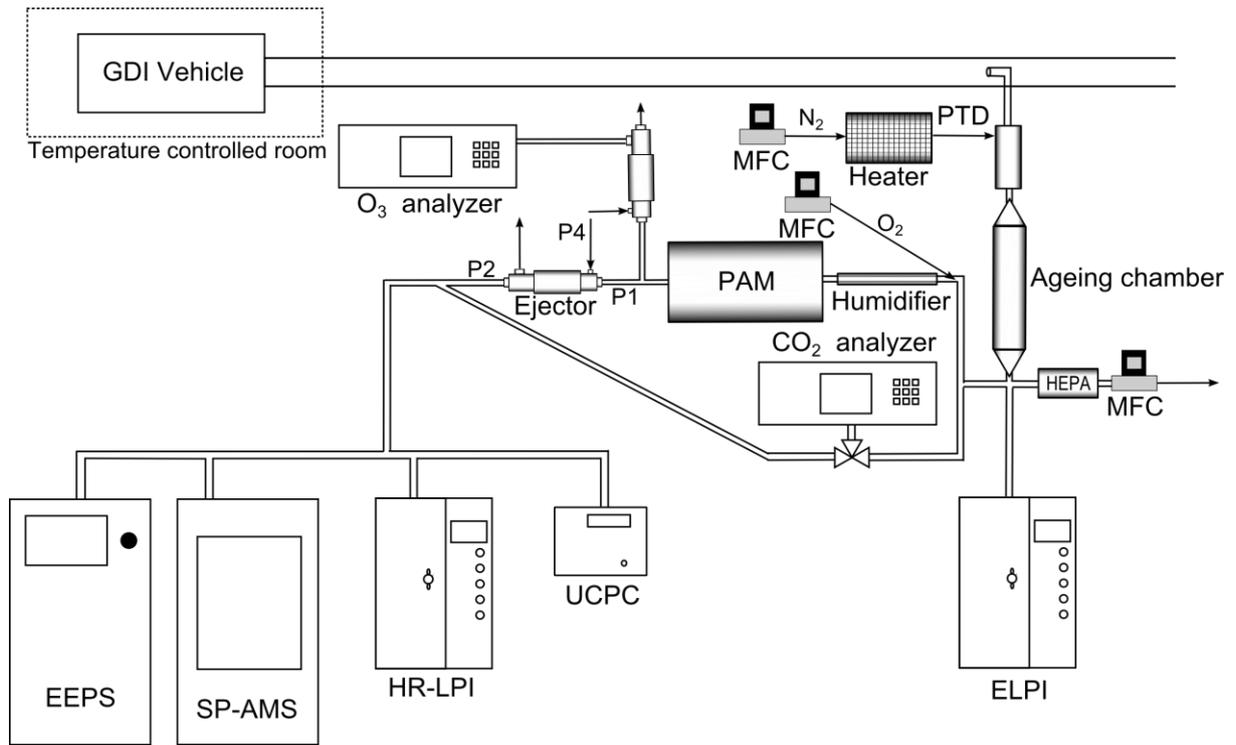
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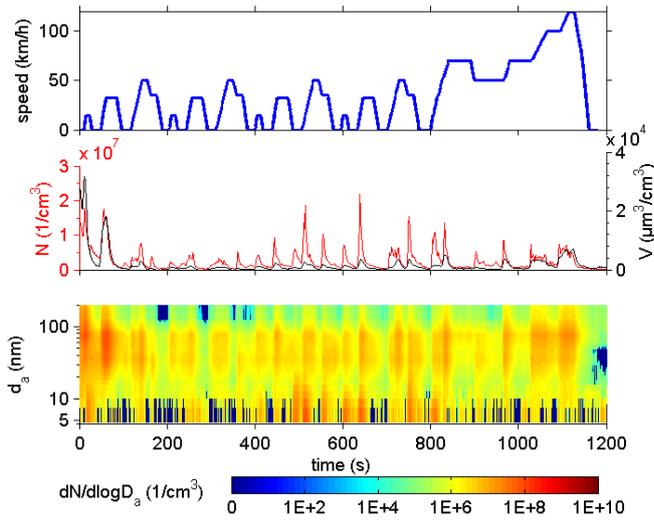
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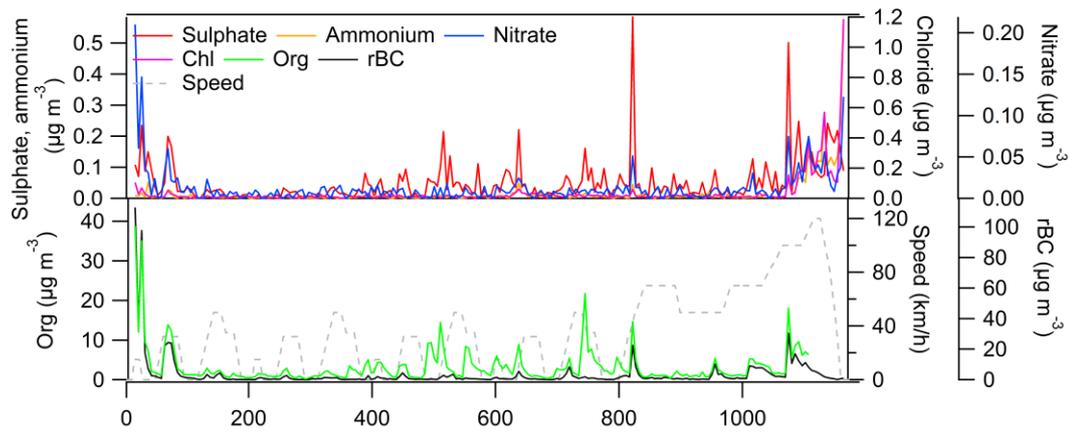
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Figure 1. Schematic of the experimental setup (MFC = mass flow controller).



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Figure 2. Speed profile, primary particle number (measured by the CPC) and volume concentrations (measured by HRLPI) and primary particle size distributions (HRLPI) for the studied gasoline passenger car during the NEDC test cycle.



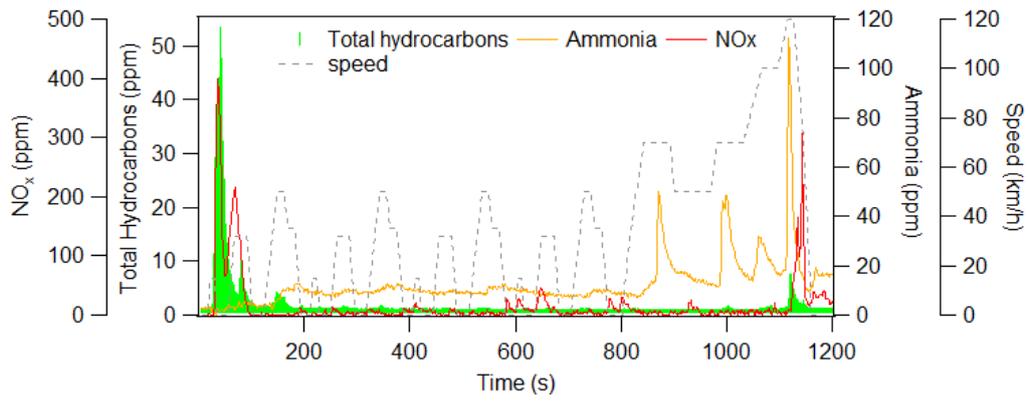
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3 Figure 3. Temporal behavior of rBC, organics, SO₄, NO₃ and NH₄ concentrations measured
 4 by the SP-AMS for the primary emissions (without the PAM chamber) during the NEDC test
 5 cycle.

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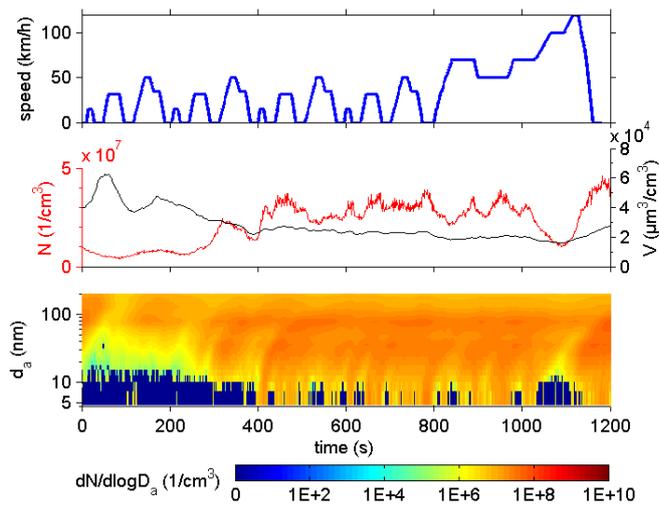
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2 Figure 4. Time-series of the exhaust concentrations of total hydrocarbons, ammonia and NO_x.

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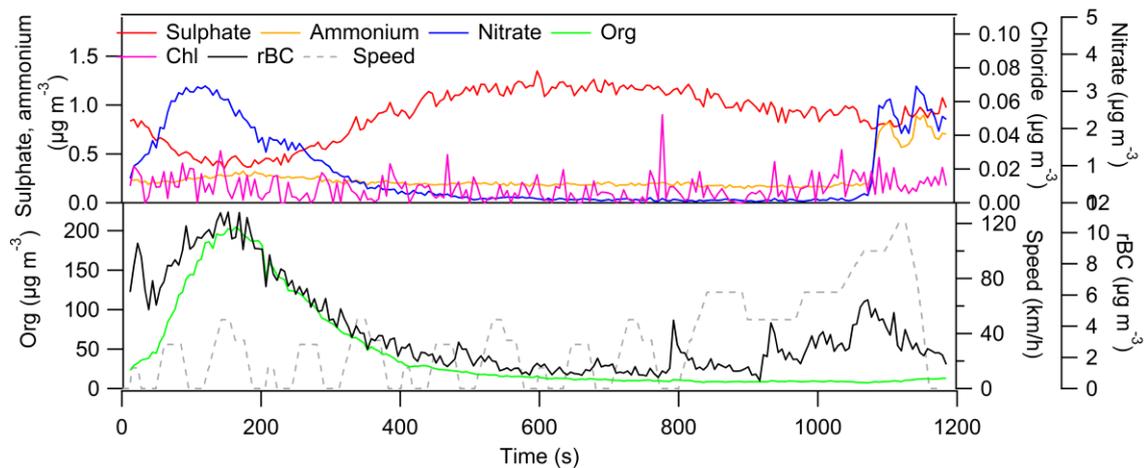


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3 Figure 5. Speed profile, secondary particle number (measured by the CPC) and volume
 4 concentrations (measured by the HRLPI) and secondary particle number size distributions
 5 (HRLPI) for the studied gasoline passenger car during the NEDC test cycle.

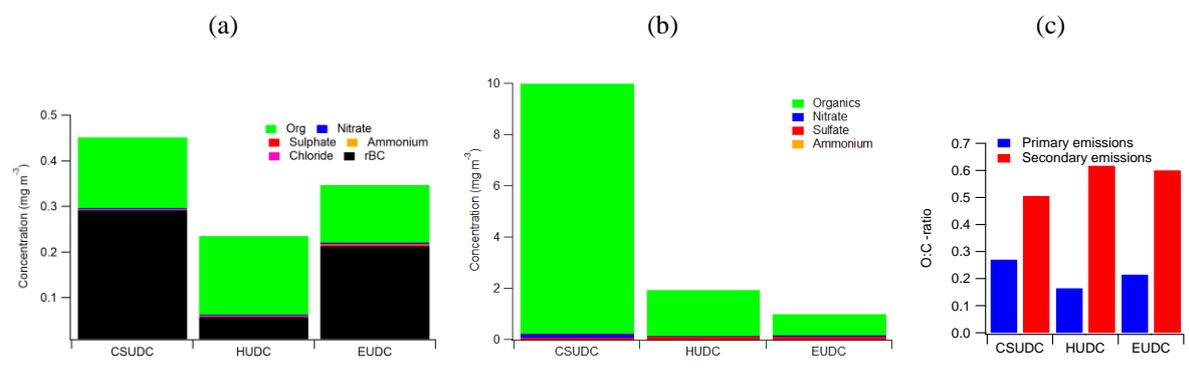
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Figure 6. Temporal behavior of rBC, organics, SO₄, NO₃, NH₄ and Cl concentrations measured by the SP-AMS downstream of the PAM chamber during the NEDC test cycle.

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4 Figure 7. (a) Chemical composition of primary PM, (b) chemical composition secondary PM,
5 and (c) the O:C -ratios of primary and secondary particulate matter for different parts of the
6 NEDC cycle.