Influence of fuel ethanol content on primary emissions and secondary aerosol formation potential for a modern flex-fuel gasoline vehicle

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Abstract

The effect of fuel ethanol content (10%, 85%, 100%) on primary emissions and on subsequent secondary aerosol formation was investigated for a EURO5 flex-fuel gasoline vehicle. Emissions were characterized during the New European Driving Cycle (NEDC) using a comprehensive setup of high time resolution instruments. Detailed chemical composition of exhaust particulate matter (PM) was studied using a soot particle aerosol mass spectrometer (SP-AMS) and secondary aerosol formation using a potential aerosol mass (PAM) chamber. For the primary gaseous compounds, an increase in total hydrocarbon emissions and a decrease of aromatic BTEX (benzene, toluene, ethylbenzene and xylenes) compounds was observed when the amount of ethanol in fuel increased. In regard to particles, largest primary particulate matter concentrations and potential to form secondary particles were measured for the E10 fuel (10% ethanol). As the ethanol content of the fuel increased, a significant decrease in average primary particulate matter concentrations over the NEDC cycle was found, PM emissions being 0.45, 0.25 and 0.15 mg m^{-3} for E10, E85 and E100, respectively. Similarly, a clear decrease in secondary aerosol formation potential was observed with larger contribution of ethanol in fuel. Secondary to primary PM ratios were 13.4, and 1.5 for E10 and E85, respectively. For E100 a slight decrease in PM mass was observed after the PAM chamber, indicating that the PM produced by secondary aerosol formation was less than the PM lost via e.g. wall losses or degradation of POA in the chamber. For all fuel blends, the formed secondary aerosol consisted mostly of organic compounds. For E10 the contribution of organic compounds containing oxygen increased from 35%, measured for primary organics, to 62% after the PAM chamber. For E85 the contribution of organic compounds containing oxygen increased from 42 % (primary) to 57% (after the PAM chamber), whereas for E100 the amount of oxidized organics remained the same (approximately 62%) with the PAM chamber when compared to the primary emissions.

1. Introduction

Vehicular engine emissions are known to degrade air quality in urban areas. Besides gaseous compounds (e.g. CO, NO_x, hydrocarbons, volatile organic compounds), vehicle exhaust contains significant amounts of primary particulate matter (PM) (e.g. Maricq, 2007; Keuken et al., 2013; Gordon et al., 2014a). Primary particulate matter refers to particles directly emitted

5   e.g. from engine, fuel combustion process or brakes, and not yet experienced any significant chemical transformation in the atmosphere. Depending on engine and fuel type, primary exhaust PM emissions from vehicles consist mainly of soot and different fuel and lubricating oil components (Maricq, 2007; Canagaratna et al., 2010; Karjalainen et al., 2014). In addition to primary PM, burning process in engine cylinder produces so called delayed primary aerosol species like sulfuric acid which are in tailpipe conditions in gaseous phase but will condense or nucleate immediately when the exhaust is cooled and diluted,

10   without any significant chemical transformation in the atmosphere (Arnold et al., 2012; Rönkkö et al., 2013; Pirjola et al., 2015). In particle number size distribution the exhaust PM formed by different processes are frequently seen as separate modes with different concentrations and particle size ranges (Kittelson, 1998; Rönkkö et al., 2013). In addition to primary emissions, large amounts of secondary particulate matter forms after the exhaust gases are released into the atmosphere (Chirico et al., 2010). While a large number of studies have focused on vehicular primary particulate emissions (Giechaskiel et al., 2005;

15   Maricq, 2007; Lähde et al., 2010; Karjalainen et al., 2014) relatively limited number of studies have focused on secondary emissions.

Both batch chambers (such as smog chambers) and flow through chambers have been used to study vehicular secondary aerosol emissions in both laboratory and ambient conditions. A batch chamber is good for detailed oxidation process studies (e.g. Chirico et al., 2014; Suarez-Bertoa et al., 2015), but cannot be used to differentiate rapidly changing driving conditions during

20   the test driving cycle. Flow through chambers such as Potential aerosol mass (PAM) chamber are designed to simulate secondary aerosol mass formation potential on a close to real-time basis (Kang et al., 2011; Lambe et al., 2011). Recent chamber studies have shown that Secondary particulate emissions from the combustion engines consists mainly of organic compounds and ammonium nitrate (Nordin et al., 2013; Karjalainen et al., 2015; Suarez-Bertoa et al., 2015) and that the secondary PM emissions can be significantly larger than primary emissions if conditions favours secondary aerosol formation

25   (Giechaskiel et al., 2005; Chirico et al., 2010; Karjalainen et al., 2015). In gasoline vehicles exhaust emissions of secondary aerosol precursors have been shown to depend e.g. on driving conditions, fuels and operation of catalytic converter (Durbin et al., 2007; Maricq et al., 2012; Gordon et al., 2014b; Karjalainen et al., 2015). Also, previous studies indicate that gasoline vehicles have an impact on secondary aerosol concentrations in urban areas (Nordin et al., 2013; Tkacik et al., 2014; Karjalainen et al., 2015; Suarez-Bertoa et al., 2015). However, the secondary aerosol formation potential and composition as

30   a function of driving situation for different ethanol content fuels (E10-E100) are poorly characterized in the literature.

Secondary particulate matter forms in the atmosphere via gas-to-particle conversion as oxidation process typically lowers the volatility (vapour pressure) of gaseous compounds. The hydrocarbons of gasoline typically includes 4-12 carbon atoms with boiling range between 30 and 210 °C. (Owen and Coley 1995). These may be present in the exhaust gases as unburned hydrocarbons. In addition, exhaust gases contain compounds formed in combustion and those originating from engine oil.

5 Lipari et al. (1990) analysed 103 individual hydrocarbons up to C12 in a study with FFV using gasoline and methanol containing fuels M85 and M100. For gasoline, toluene, ethylene, propylene, isobutylene, isopentane, pentane, benzene and iso-octane represented 55% of THC. These gaseous compounds are emitted into atmosphere directly or they are evaporated from primary exhaust particles when the exhaust is diluted (Robinson et al., 2007). Oxidation products of organic compounds may contain one or more functional groups such as alcohol (-OH), aldehyde (-CHO), carboxylic acid (–COOH), nitro (-NO_2)

10 and nitrate (-NO_3) or organic sulfate (-OSO_3) groups. Ambient photochemical reactions take place in the presence of NO_2, VOCs, heat and sunlight. Hundreds of different VOC species can participate in thousands of photochemical reactions (Drechsler 2004). Different possible photo-oxidation pathways are also depending on conditions. E.g. for aromatic BTEX (BTEX = benzene, toluene, ethylbenzene, and xylenes; volatile organic compounds (VOC) typically found in petroleum derivates) compounds have been suggested to depend on, for example, prevailing NO_x concentrations (Andino et al., 1996;

15 Hurley et al., 2001; Sato et al., 2007; Sato et al., 2012). Sato et al. (2007) found aromatic and ring-cleavage products from the photo oxidation of toluene, tentatively assigned to C_7 unsaturated oxacyclic oxocarboxylic acids and dicarboxylic acids. The hemiacetal oligomers and/or the decomposition products of peroxy hemiacetal oligomers were also detected.

European Union has set an obligation that the share of renewable energy should be at least 10% in the transportation sector by 2020 (Directive 2009/28/EC). Ethanol is the dominant bio-component in transport fuels worldwide. However, in Europe its

20 share in gasoline is limited to 10 vol-%, which is equivalent to approximately 6% energy content [Directive 2009/30/EC]. Higher ethanol concentrations up to 85 vol-% (E85) can be used in special flex-fuel vehicles (FFVs). Previous studies have shown that typically, primary PM, CO, HC, NO_x and aromatic hydrocarbon emissions are lower for the E85 fuel than for gasoline, whereas ethanol, acetaldehyde, formaldehyde and methane emissions increase with increasing ethanol content of gasoline (Yanowitz et al.; Nylund and Aakko, 2003; Karlsson et al., 2008; Westerholm et al., 2008; Clairotte et al., 2013). In

25 order to reduce the detrimental effects of pollution caused by vehicles, the emission standards for PM emissions of vehicles are getting tighter globally. However, it must be noted that in the emission standard laboratory tests the PM mass is measured directly after the tailpipe from a filter sample at elevated temperature and thus represents mainly primary non-volatile PM emissions. As the previous studies have demonstrated (e.g. Chirico et al., 2010; Nordin et al., 2013; Platt et al., 2013; Suarez-Bertoa et al., 2015), the secondary PM emissions, formed from gaseous precursors, can be significantly larger than primary

30 PM emissions, meaning that the emission limits do not necessarily regulate secondary PM emissions.

In order to properly quantify vehicular engine emissions, the whole transformation chain from freshly emitted primary PM and gaseous compounds to aged secondary PM measured in urban air quality stations has to be better understood. The main

objective of this study was to investigate primary particulate emissions and simulate the secondary aerosol formation potential of vehicular emissions with an oxidation flow chamber when the ethanol content in fuel increases. Measurements were carried out with a modern FFV using fuels with three different ethanol contents (10%, 85% and 100%). A comprehensive set of instruments were used for measuring gaseous emissions together with chemical composition and size distributions of primary

5   and secondary particles. All measurements were done with the high time resolution instruments and with the potential aerosol mass (PAM) flow-through oxidation chamber. The used measurement setup enabled the characterization of concentration and composition changes during different parts of the driving cycle.

2. Experimental

2.1 Measurement setup and sampling

10   The measurement setup of this study is described in detail by Karjalainen et al., 2015. Article made by Karjalainen et al., 2015 is focused to primary and secondary emissions of a flex-fuel vehicle using E10 fuel, whereas this article is focused on influences of fuel alcohol content to particulate and gaseous emissions and their composition. Shortly, emissions from a flex-fuel passenger car (model year 2011, 1.4 liter turbo charged direct injection spark ignition (DISI) engine, EURO5) were measured on a chassis dynamometer at 23°C using three different fuels (E10, E85, E100). The driving cycle was New European

15   Driving Cycle (NEDC). NEDC cycle consists of three parts with different engine and speed profiles; First urban driving cycle (UDC) is repeated twice, first part represents urban driving cycle with a cold start (0-391 s, CSUDC), second represents typical urban driving (392-787s, HUDC) and last part represents highway driving (788-1180s, EUDC). NEDC cycles were run in separate days in order to enable cold start conditions for each fuel. Test fuels comprised of a regular commercial E10 (max 10% ethanol), E85 (85% ethanol), and E100 (100% ethanol). Deionized water was added into E100 to adjust water content to

20   4.4 % (m/m). Particle sampling was conveyed by partial exhaust sampling system (Ntziachristos, 2004) at the exhaust transfer line. The sampling system consisted of a porous tube diluter (PTD, dilution ratio DR = 12), residence time chamber (2.5 s) and secondary dilution conducted by a Dekati Diluter (DR = 8). Regarding particle formation by nucleation, the sampling system mimics exhaust dilution and nanoparticle formation processes in the atmosphere (Rönkkö et al., 2006; Keskinen and Rönkkö, 2010).

    The PAM chamber was used to evaluate secondary aerosol formation potential during the NEDC driving cycle. The PAM chamber is a small, flow-through chamber that is irradiated with ultraviolet light (wavelengths 185 and 254 nm) to form high concentrations of oxidants (O_3, OH, HO_2) that can initiate the production of secondary aerosol particles (Kang et al., 2007; Kang et al., 2011, Lambe et al., 2011). High oxidant concentrations (up to 1000-fold to atmosphere, with the same oxidant ratios as in the atmosphere) and high UV lights assure the fast oxidation of compounds (Kang et al., 2007). The aging as the

30   sample flows through the chamber is shown to represent up to several weeks of aging in the atmosphere (Kang et al., 2011; Ortega et al., 2013). The PAM chamber has been thoroughly characterized in previous studies. These studies include loss

characterization, comparison to other chambers studies as well as comparison on how SOA formed in chamber compares to SOA observed in ambient atmosphere and SOA produced in large environmental chambers as well (See e.g. Kang et al., 2007; Kang et al., 2011; Lambe et al., 2011; Tkacik et al., 2014; Lambe et al., 2015; Peng et al., 2016). The PAM chamber used in this study is described in detail by Karjalainen et al., 2015. Shortly, the PAM chamber was installed between the residence

5   time chamber and secondary dilution unit of sampling system. The particle instrumentation was located downstream of the secondary diluter. The sample flow through the PAM chamber was set to 9.75 l min^{-1} resulting average residence time of 84 s. The voltage of the two UV lamps was at maximum value, 190 V. The sample conditions during the test were fairly stable, typically relative humidity was 60%, temperature 22 °C and ozone concentration 6 ppm. All cycles were first run without the PAM chamber to measure primary emissions and next with the PAM chamber in order to study the formation of secondary

10   particles.

The PAM chamber was calibrated following the procedure described by Lambe et al. (2011). According to this off-line calibration, the upper limit average OH exposure during the experiments was 1.0×10^{12} molec. cm^{-3} s, corresponding to atmospheric aging of 8 days (assuming an average OH concentration of 1.5×10^6 molec. cm-3 (Mao et al., 2009)), but the real

15   OH exposure was lower due to high concentrations of OH reactive gases in the exhaust. The effect of OH reactive emissions on the PAM OH exposure is evaluated with the calculator tool developed by Peng et al. (2016) using the measured VOCs (chapter 2.3) and CO as the input parameters. This effect was significant especially at the beginning of the cycle (CSUDC) when the VOC concentrations were high. The external OH reactivities (OHR) in CSUDC were 910 s^{-1}, 1009 s^{-1} and 12500 s^{-1} for E10, E85 and E100, respectively. Using the calculator by Peng et al. (2016), the corresponding OH exposures were

20   approximately 1 equivalent days for E10 and E85, and 0.02 days for E100. The higher OHR of E100 was due to high ethanol and aldehyde concentrations. After the CSUDC, OHR was below 45 s^{-1} for E10 and E85, implicating that the OH exposure was close to the upper limit (8 equivalent days). When using E100 fuel, the OHR was approximately 300 s^{-1} after the CSUDC, which gives an OH exposure of approximately 3.4 days. Thus, the secondary aerosol formation measurements for E100 are not directly comparable to those of the other fuels, particularly at the beginning of the cycle. More detailed OHR calculations

25   are shown in Tables S1-S3. We note that the calculator results should be considered only as estimates since they are not verified by laboratory measurements for this particular chamber. However, the results can be used to compare the relative differences in OH exposures between the cycles.

2.2. Particle measurements

30   The Soot Particle Aerosol Mass Spectrometer (SP-AMS, Aerodyne Research Inc., US) was used to measure the chemical composition of emitted PM. The SP-AMS is a high resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) with added laser (intracavity Nd:YAG, 1064 nm) vaporizer. Dual vaporizer system enables the real-time measurements of PM mass and size-resolved chemical composition of submicron non-refractory particulate matter, refractory black carbon and some

metals and elements. The HR-ToF-AMS is described in detail by Jayne et al. (2000); and DeCarlo et al. (2006) and the design of the SP-AMS by Onasch et al. (2012). Briefly, in the SP-AMS an aerodynamic lens is used to form a narrow beam of particles that is transmitted into the detection chamber. Particles are vaporized either by tungsten vaporizer (600 °C) to analyze non-refractory inorganic species and organics and/or with the SP laser (intracavity Nd:YAG, 1064 nm) in order to analyze refractory

5   black carbon (rBC) and metals in addition to inorganics and organics attached to these particles. The vaporized compounds are ionized using electron impact ionization (70 eV) and formed ions are guided to the time-of-flight chamber and to the multi-channel plate (MCP) detector. A five second averaging time was used in the AMS measurements. The collection efficiency (CE) value, representing the fraction of sampled particle mass that is detected by the MCP detector, is required for the calculation of aerosol mass concentration measured by the AMS. The previous studies have shown that the collection efficiency

10   of an aerosol mass spectrometer is affected by particle losses (i) during transit through the inlet and lens, (ii) by particle beam divergence for both tungsten and laser vaporizers and by (iii) bounce effects from tungsten vaporizer (Matthew et al., 2008; Huffman et al., 2009; Onasch et al., 2012). Similar to Karjalainen et al. (2015) a CE = 1 was used in this study for all SP-AMS data. We acknowledge that it is likely that the collection efficiency might be underestimated for thinly coated, primary emissions whereas used CE = 1 is likely closer to correct value for than for heavily coated spherical secondary aerosol. Also,

15   we note that collection efficiency for gasoline soot, consisting of agglomerates with average diameter below 90nm, will likely have low transmission efficiency in aerodynamic lens and thus might have lower collection efficiency than regal black.

The particle number size distributions were measured using a time resolution of 1 Hz with a High-Resolution Low-Pressure Cascade Impactor (HR-LPI; Arffman et al., 2014) and an Engine Exhaust Particle Sizer (EEPS, TSI Inc.; Mirme, 1994; Johnson, 2004). The particle number concentration was also measured with an ultrafine condensation particle counter (UCPC,

20   TSI Inc. model 3025). The UCPC was located downstream of an additional diluter (operation principle based on the partial filtration of the sample, DR = 42) to ensure that the concentrations to be measured are within its measurement range. All the data shown below has been corrected by a total dilution ratio for each instrument, thus the presented values represent the tailpipe concentrations.

25   **2.3. Gaseous phase composition measurements**

Total hydrocarbon (THC) concentrations were measured with a flame ionization detector (FID) developed for the standardized exhaust emission test procedures of cars. The FID detects all carbon-containing compounds, for example carbonyl compounds, in addition to hydrocarbons (HC; Sandström-Dahl et al., 2010). In addition, samples were collected using Tedlar bags for subsequent analysis by a gas chromatograph (HP 5890 Series II, AL2O3, KCl/PLOT column, an external standard method).

30   The analysed hydrocarbons (from C_1 to C_8) included methane, ethane, ethene, propane, propene, acetylene, isobutene, 1,3-butadiene, benzene, toluene, ethyl benzene and m-, p- and o-xylenes. Total hydro carbons (THC) measured with a FID accounts for all carbon-containing compounds, also oxygenates such as alcohols and carbonyl compounds (Sandström-Dahl et al. 2010 and Aakko-Saksa et al. 2014). In these measurements, the sum of HCs analysed by GC and HC portions of ethanol and

acetaldehyde resulted in HC sum of 15 mg/km for E10, 30 mg/km for E85 and 216 mg/km for E100. The respective THC (FID) results were 22 mg/km, 30 mg/km and 193 mg/km. This indicated that on average 73% of THC (FID) were analysed for E10, and 100 % for E85 and E100 by the GC, FTIR and HPLC analyses.

5 Besides HCs, selected aldehydes were analysed by collecting diluted exhaust gas samples from the Constant Volume Sampler (CVS) using 2,4-dinitrophenylhydrazine (DNPH) cartridges. The DNPH derivatives were extracted with an acetonitrile/water mixture and analysed using HPLC technology (Agilent 1260, UV detector, Nova-Pak C18 column). Aldehydes analysed include formaldehyde, acetaldehyde, acrolein, propionaldehyde, crotonaldehyde, methacrolein, butyraldehyde, benzaldehyde, valeraldehyde, m-tolualdehyde and hexanal. Ethanol and a number of other compounds were measured on-line using Fourier
10 transformation infrared (FTIR) analyzer (Gasmet Cr-2000).

3. Results

The following chapters describe the gaseous emissions, primary and secondary particulate emissions for fuels with different ethanol content (E10, E85, E100). In addition, secondary to primary PM –ratios, time trends of different species during the driving cycle as well as elemental composition of primary and secondary emissions for different ethanol content fuels are
15 studied.

3.1. Gas phase emissions

The composition of gas phase emissions was observed to change when the ethanol content of the fuel changed (Fig. 1). As the ethanol content increased a clearly detectable decrease was observed in both average NO_x and ammonia concentrations during the measurement cycle. Decrease in NO_x with increasing ethanol content is likely caused by decreased flame temperature
20 (Turner et al., 2011). For instance Turner et al., 2011 reported a decrease of about 20 to 40 °C in exhaust temperature of a DISI engine when the ethanol content of fuel changed from 0 to 100%. Simultaneously, they reported that the NO_x emission decreased even from 8 g/kWh to 0.5 g/kWh, both values slightly depending also on ignition timing and strategies. Decreasing trend in the NOx emissions have been observed also by Maricq et al. (2012) who report the decreases of 20% in NOx emissions when the ethanol content increases to values more than 17%.

25 Ammonia is formed in the reactions of the three-way catalyst (Mejia-Centeno et al., 2007). In theory, ammonia formation is enhanced in slightly rich air-to-fuel ratio at high temperatures (aggressive accelerations) when sufficient HC and NOx concentrations are present (Heeb et al., 2006; Mejia-Centeno et al., 2007; Li et al., 2010). Engine-out emissions were not measured here, but it is assumed the HC and NOx concentrations were not a limiting condition for ammonia formation. Decrease in the ammonia emissions for the E85 fuel indicates an enleanment of the conditions in the TWC catalyst when
30 compared with those for the E10 fuel. Clairotte et al. (2013) also reported of lower ammonia emissions for the E85 fuel than

for the E5 fuel. The decreases in both ammonia and NOx leads to a decreased contribution to secondary aerosol formation of ammonium nitrate in the atmosphere when increasing the ethanol content.

The amount of hydrocarbon emissions typically depends on combustion conditions and exhaust after-treatment by catalytic devices. In this study, the test vehicle was equipped with a three-way catalytic converter, with an effectivity which depends on exhaust temperature and also on properties of hydrocarbons. In this study the composition of hydrocarbon emissions were observed to be strongly dependent on the ethanol content; as the ethanol content increased in fuel, short chain non-aromatic hydrocarbons and aldehydes increased in the exhaust, while a decreasing trend was observed for all measured aromatic hydrocarbon compounds. Also as the ethanol content of fuel increased, the exhaust concentrations of formaldehyde, acetaldehyde, ethanol, methanol, ethene and acetylene increased whereas the exhaust concentrations of NO_x, ammonia, PM and BTEX decreased (Fig. 1).

3.2. Composition of primary particulate matter emissions

The chemical composition of primary particulate emissions was observed to vary for different fuels (Fig. 2, Composition in units mg/km for both primary and secondary emissions is shown in the supplement Fig S1). For E10 approximately half of primary PM emissions was rBC and the other half was organics. The contribution of inorganic species (sulfate, nitrate, ammonium, chloride) to PM mass was small (1.2 %). Of inorganic ions, sulfate had the highest contribution (47–67% of mass of inorganic ions) for all fuels. A clear decrease in rBC concentration and in its contribution to total emitted primary PM was observed as the ethanol content of fuel increased (E10, BC: 53%, E85, BC: 31%, E100, BC: 25%), whereas contribution of organic matter increased from 46% (E10) to 65% for E85 and 75% for E100. Organics to rBC –ratios for the E10, E85 and E100 were 0.9, 2.1 and 3.1, respectively.

Figure 3 shows the elemental ratios (oxygen to carbon: O:C and hydrogen to carbon: H:C) for primary organic PM. All values are average values over the NEDC cycle. Average elemental composition and elemental ratios (O:C, H:C) are calculated using method developed by Aiken et al. (2007) where elemental composition is calculated using all measured fragment ions observed in high-resolution mass spectra and H:C and O:C calibration factors derived from laboratory measurements of standard organic molecules. Canagaratna et al., 2015 further developed elemental analysis to contain a wider range of OA species that are more representative of ambient OOA species. Improved ambient ratios (IA) calculated according to method published by Canagaratna et al., 2015 are also shown in Figure 3. Rather similar O:C –ratios (0.35–0.4) were observed for the primary organic fraction for all fuels. Observed H:C ratio for primary emissions of E10 and E85 (~1.5) was slightly lower than for E100 (1.7). Observed elemental ratios are comparable to elemental ratios typically observed for hydrocarbon-like organic aerosol (HOA) representing traffic emissions in ambient atmosphere and elemental ratios observed in chamber studies (Tkacik et al., 2012; Timonen et al., 2013; Carbone et al., 2014; Canagaratna et al., 2015). We note that these O:C –ratios measured with a SP-AMS can be slightly higher than ratios typically measured with a AMS for primary emissions from gasoline vehicles due to the fact that SP-AMS detects also refractory organic species (rCOx) incorporated on the structures of black carbon particles (Corbin et al., 2014).

3.3. Composition of secondary aerosol simulated with a PAM chamber

Secondary aerosol formation in the PAM chamber increased the contribution of both organic and inorganic compounds (Fig. 4). For all fuels most of the particulate matter observed after the PAM chamber (E10; 89%, E85: 79%, E100: 61%) consisted of organic compounds. Organics to rBC –ratios for the secondary emissions of E10, E85 and E100 were 12, 8.3 and 3.1, respectively. The main inorganic ions observed after PAM chamber were nitrate, sulphate and ammonium. When the ethanol content of fuel increased, the relative contribution of inorganic ions (E10: 4 %, E85: 12% , E100: 19 %) in exhaust PM increased after the PAM chamber.

3.3.1 Organic aerosol

Figure 5 shows the average elemental ratios over the NEDC cycle calculated for organics from the SP-AMS data. For E10 increase in O:C (from 0.4 to 0.6) and a decrease in H:C –ratio (from 1.55 to 1.45) was observed when the PAM chamber was used. In contrast, no change in O:C or H:C –ratio was observed for E85 when using the PAM chamber. For E100, a slight decrease in O:C and H:C –ratios was observed when using the PAM chamber. Similar elemental ratios (O:C 0.4–0.7) (Nordin et al., 2013; Suarez-Bertoa et al., 2015) have been observed for secondary PM emissions in previous batch chamber studies. As shown for the gaseous exhaust compounds (chapter 3.1), the composition and concentrations of gaseous precursors change when the ethanol content of fuel increased, causing also a clear change in observed secondary aerosol and its oxidation state.

Figure 6 shows the contribution of different organic fragments C_xH_y (hydrocarbons $C_xH_y^+$), C_xH_yO (fragments with one oxygen atom $C_xH_yO^+$ e.g. CO^+ and CHO^+) and $C_xH_yO_z$ (compounds containing several oxygen atoms $C_xH_yO_{z,\ z>1}^+$ e.g. CO_2^+) for all the fuels with and without the PAM. The contribution of $C_xH_yO^+$ to organics increased after the oxidation of exhaust sample in the PAM chamber for all the fuels whereas the contributions of $C_xH_yO_{z,\ z>1}^+$ and $C_xH_y^+$ decreased. For E10 the contribution of the sum of oxidated compounds ($C_xH_yO^+$ and $C_xH_yO_z$) on exhaust PM was increased from 35% to 62%. For E85 the contribution of oxidized organic compounds increased from 42 to 57%, whereas for E100 the contribution of oxidized organic compounds (approximately 62%) remained the same with PAM chamber when compared to primary emissions.

3.3.2 Refractive Black carbon

Refractive Black carbon (rBC) is formed in incomplete combustion and is always considered primary emission, therefore the rBC concentrations with and without the PAM chamber should be the same. However, some differences in rBC concentrations were observed when primary rBC concentrations were compared to the rBC results measured after the PAM chamber. For E85 and E100 a slight decrease in rBC after the PAM chamber was observed (20-30%). This decrease is likely explained by losses of primary PM in the chamber. Karjalainen et al., 2015 showed that the particle losses in PAM chamber were on similar level as BC losses seen for here (approximately 8-30% for particle sizes 50 nm-400 nm). However, in contrast, for E10 a clear increase in rBC (from 240 μg m^{-3} to 480 μg m^{-3}) was observed when the emissions during driving cycle were measured with

the PAM chamber. In the SP-AMS rBC is calculated as a sum of carbon fragments C_x^+. To explore the increase in BC after the PAM chamber, the C_x fragments before and after the PAM chamber were studied for E10. The increase after the PAM chamber for E10 was seen in all C_x fragments (Fig. S2; w PAM / w/o PAM –ratios from 1.6 to 2.8 for C_2-C_5 fragments). The main fragments C_3^+ and C_2^+ of rBC (contributions 59% and 27%, respectively) did not have any major interference from

5   isobaric ions (ions observed in same nominal mass). Larger fragments (e.g. C_5^+-C_9^+) had interfering isobaric organic compounds, but their contribution to total mass was less than 10% and the influence of interference was therefore considered to be unsignificant. Previous studies have shown that the soot particles emitted by DISI vehicles are small, typically on the size range of 10-100 nm (Karjalainen et al., 2014). Due to restrictions of aerodynamic lens, particles smaller than 50 nm are not effectively detected by the SP-AMS. Also must be noted that the PM losses in the PAM chamber are depending on the

10   particle size, the largest losses up to 60% are seen for particles with Dp < 50nm. Difference in the rBC results for E10 between primary emissions and emissions after the PAM is likely partly explained by increased mean particle size due to SOA formation increasing the efficiency particles are detected by the SP-AMS (low volatility compounds formed in the PAM chamber condense on the surfaces of soot particles increasing their aerodynamic size and thus the detection efficiency of soot/rBC). Also, Willis et al. (2014) demonstrated that the thick coating increases the collection efficiency via changing the particle

15   morphology and thus decreasing the beam divergence and increasing the particle and laser beam overlap. Based on increase in mean particle size and secondary to primary PM -ratios it can be assumed (see also chapter 3.4, and size distributions with and without PAM chamber figures S3,S4) that for E10 the soot particles are heavily coated with SOA after the PAM chamber and thus they are more effectively detected by the SP-AMS. In contrast, it has been shown that dispersion of small and nonspherical particles in the aerodynamic lens inlet of the SP-AMS may cause particles to miss the laser vaporizer (Onasch et

20   al., 2012). Based on the previous studies, it is known that black carbon particles emitted by engines are typically agglomerates with irregular shape and diameter 10-90 nm (Happonen et al., 2010; Lähde et al., 2010; Karjalainen et al., 2014; Liati et al., 2016), which also might decrease the detection efficiency of primary black carbon (soot) particles. We also note that the losses for PM in the PAM chamber are depending on particle size, the smaller the particles are, the larger the losses are (Karjalainen et al., 2015).

3.3.3 Inorganic ions

In comparison to organics, observed inorganic ion concentrations after the PAM chamber were from moderate to low (ion contribution to PM mass E10: 3.8%, E85: 12% and E100: 19%). The main ions observed after PAM chamber were sulphate, nitrate and ammonium for all fuels. In this study the sulphur content of E10 fuel was smaller than 10 ppm and for E100 close to zero (below detection limit of our fuel analyses). These facts suggest strongly that, especially for E100, most of the observed

30   sulphate emissions originates from lubricant oil.

3.4. Primary to secondary particulate matter -ratios

Table 1 and Figure 7 shows the submicron PM concentration for both primary emissions and for potential secondary aerosol emissions measured after the PAM chamber averaged over the driving cycle. PM was calculated as a sum of all SP-AMS species in the size range of the SP-AMS (30–800 nm). PM concentration measured after the PAM chamber is a sum of both primary particulate emissions and formed secondary aerosol. Secondary aerosol concentrations were calculated by subtracting the concentrations of primary particles from the PM concentrations observed after the PAM chamber. It is likely that wall losses in the chamber will somewhat decrease primary aerosol concentrations and thus might increase the observed secondary to primary PM –ratio when particles go through the PAM chamber. Also one has to note that it is likely that in the PAM chamber new material originating from gaseous phase will condense on existing particles, which can change the particle morphology, increase the particle size and furthermore change their detection efficiency in the SP-AMS (Onasch et al., 2012; Willis et al., 2014) thus slightly also affecting observed secondary to primary PM ratios.

Large differences in the concentrations between primary and secondary emissions were observed for different ethanol content fuels. The largest primary and secondary PM concentrations were observed for E10 (0.45 mg m^{-3} for primary PM and 6.7 mg m^{-3} after PAM chamber). A clear decrease in primary PM emissions (E85; 0.24 mg m^{-3}, E100: 0.15 mg m^{-3}) were seen as the ethanol content in fuel increased. Similar to our results, Maricq et al. (2012) observed a decrease in primary PM concentrations when ethanol content of fuel increased, however they did not measure the secondary aerosol formation potential. The ethanol content of fuel had also a large influence on the secondary aerosol formation potential. For E10 PM measured after the PAM chamber was on average 14.7 times larger than the primary PM. For E85 the secondary PM emissions after the PAM chamber were on average approximately two times larger (0.62 mg m^{-3}) than primary PM emissions and for E100 a slight decrease in PM mass (E100: 0.12 mg m^{-3}) was seen after PAM chamber, indicating that either the secondary aerosol formation was insignificant (Fig. 2, Table 1) or extensive fragmentation decreased observed PM mass. Previous studies (e.g. Tkacik et al., 2014) have shown that high OH exposures cause reduction in the observed mass because of fragmentation, which forms light organic compounds that are more volatile and will evaporate from the particulate phase. In the case of E100, the fragmentation probably does not occur at the beginning of the cycle because of the low OH exposure. Corresponding secondary to primary PM ratios were 13.4 and 1.5 for E10 and E85, respectively.

The Influence of fuel composition on secondary aerosol formation has been studied only in a few articles. Suarez-Bertoa et al. (2015) has studied the exhaust secondary aerosol formation for vehicles using high ethanol content fuels (E75, E85). They used a batch chamber in their study and found that the secondary aerosol, mostly secondary organic aerosol (SOA) was on average three times higher than primary emissions for high ethanol content fuels, however they did not measured the secondary aerosol for a standard low ethanol content fuel nor for ethanol fuel (E100). This study shows that SOA formation from high ethanol content is moderate to low when compared to low ethanol content fuel. Suarez-Bertoa et al. (2015) also concluded that short-chain hydrocarbons could have a role in SOA formation, not only the aromatic BTEX compounds. We observed an

increase in ethanol and total hydrocarbon emissions as the ethanol content of fuel increased, however, the secondary aerosol

formation was observed to be lower for these high ethanol content fuels when compared to low ethanol content fuel (E10). In

this study, the concentrations of BTEX and secondary aerosol formation potential both decreased as the ethanol content of fuel

increased, indicating that the BTEX compounds had a large influence on secondary aerosol formation. This conclusion is in

5   line with results of Nordin et al. (2013), who found that light aromatic precursors (C6-C9) were responsible for 60% of formed

SOA in a batch type smog chamber.

Tkacik et al., (2014) studied secondary aerosol formation from in-use vehicle emissions using a PAM chamber in a highway

tunnel in Pittsburgh. Similar to our study, they observed secondary to primary PM ratios in up to 10 in the tunnel. They also

10   found that the peak in secondary aerosol production occurred conditions equivalent to 2−3 days of atmospheric oxidation and

with higher OH –oxidation values they saw a decrease in secondary aerosol formation due to continued oxidation fragmenting

carbon compounds. In E10 and E85 experiments, the atmospheric age was approximately 1 day at the beginning of the cycle,

and approximately 8 days for the latter parts of the cycles. Thus our results are likely on the lower-end compared to maximum

secondary aerosol formation potential.

15   **3.5. Predicted SOA formation**

SOA yield is defined as (Odum et al., 1996):

$$Y = \frac{\Delta M_O}{\Delta HC},$$

(1)

20   Where ΔM_O is the formed secondary organic mass and ΔHC is the reacted precursor mass. Using Eq. (1) and previously

measured yields, SOA originating from the measured VOCs can be predicted. We assumed that ΔHC equals the measured

VOC concentration before PAM, and similarly to Platt et al., (2013), we use low-NO$_x$ yields to get an upper limit for SOA

formation. The yields were following; for 1,3- butadiene 0.18 (Sato et al., 2011), for benzene 0.37 (Ng et al., 2007), for toluene

0.3 (Ng et al. 2007), for m-p-xylene 0.38 (Ng et al. 2007) and for o-xylene 0.1 (Song et al., 2007). For ethylbenzene, the SOA

25   yield of m-xylene (0.38) was used (Ng et al. 2007; Platt et al. 2013). According to (Volkamer et al., 2009), acetylene (C_2H_2)

SOA yield strongly depends on the liquid water content of aerosol. Here a value of 0.1 was assumed. The contribution of each

measured VOC on predicted SOA is shown in supplementary (Tables S1-S3, figures S5-S7). For E10, the predicted SOA mass

was 3263 µg m^{-3} (2.30 mg km^{-1}), for E85 473 µg m^{-3} (0.35 mg km^{-1}) and for E100 842 µg m^{-3} (0.62 mg km^{-1}). In line the with

measurement results, the theoretical yield calculations show the decrease in SOA formation potential as the ethanol content of

30   fuel increases. However, the measured SOA for E10 was approximately 1.8 times the predicted SOA, which implicates that

either the used yield values are too low, or that there are other VOCs or IVOCs contributing to SOA formation than the

measured ones. In contrast, for E85 the measured SOA is 30 % lower than the predicted SOA.

3.6 Temporal variation in chemical composition during the driving cycle for primary and secondary emissions.

Figure 8 and supplement figures S8-S19 shows time series of organic, inorganic ions and rBC compounds for primary emission (a) and emissions after the PAM chamber (b). The measurement setup used and the primary and secondary particulate emissions for E10 have been published previously by Karjalainen et al. (2015). Shortly, for E10 largest PM, organic, rBC and nitrate emissions were observed at the beginning of the cycle during the first acceleration (Karjalainen et al., 2015). Occasional increases were also observed during deceleration and engine braking conditions (Rönkkö et al. 2014, Karjalainen et al. 2014). At the end of the cycle, when speed was above 70 km/h, largest inorganic ion (sulphate, chloride and ammonium) emissions were observed. Moderate increase in organics and rBC were also observed at the end of the cycle.

Compared to E10, for which the highest primary organic emissions (concentration up to 48 µg m^{-3}) were observed right after cold start, for E85 and E100 the largest primary organics (concentration up to E85: 20 µg m^{-3}, E100: 9 µg m^{-3}) were measured either on the middle of the cycle or at the highway driving part at the end of cycle. Time trend of rBC emissions was similar for all fuels. Elevated rBC emissions were seen only at the beginning of cycle, and at the high-way driving part of the cycle (Figures S3, S7, and S13). Primary inorganic ion concentrations were highest during the highway driving part of the cycle for E10 and E85. For E100 primary inorganic ion levels were typically low, except some elevated spikes that were observed for sulphate.

Time series observed for secondary emissions was completely different when compared to primary emissions. For E10 and E85 cold start had dominating role in secondary aerosol formation with a clear increase after cold start in the first part of cycle (0–390 s). Similar increase at the beginning of the cycle was not observed for E100. During the second part of the driving cycle (390–780 s), secondary organic concentrations level stayed at a constant level until end of the cycle for all fuels. In contrast, for E100, organic PM concentrations measured after the PAM chamber were stable through the cycle, with no clear maxima.

The temporal behaviour of ions during the driving cycle was very different when compared to organics. After the PAM chamber, elevated nitrate concentrations were observed at the beginning of the cycle after the cold start and at the end of the cycle during highway driving part. For E85, and E100 nitrate concentrations measured after the PAM chamber were very low (Figures S8–S19). Elevated sulphate concentrations for all fuels were measured after the PAM chamber in the middle part of the cycle and at the end during the highway driving part of the cycle (Figures S2–S13). Elevated ammonium concentrations were observed at the end of cycle during the highway driving part for all fuels. The temporal behaviour of ammonium concentration was observed to be correlated with nitrate, suggesting ammonium nitrate formation. Tkacik et al. (2014) measured high ammonium nitrate concentrations (forming from NO oxidation to HNO$_3$ with subsequent neutralization with NH$_3$) exceeding SOA concentrations by a factor of 2 in measurements conducted in a highway tunnel. In this study the average contribution of ions to submicron PM mass was always below 20 % and the contribution of ammonium nitrate was always significantly lower when compared to SOA.

3.7. Temporal variation in size distributions of primary and secondary PM

Number size distributions of emitted particles were measured in order to understand changes in particulate phase when the driving conditions such as speed and engine load change. Figure 9 shows number size distributions of primary particles for each fuel as a function of time during the driving cycle. It can be seen that for E10 fuel the emissions of particles at the size

5   range of 30–90 nm (D_p) were higher than for E85 and E100. The emissions of the particles at the size range of 30-90 nm were depending on the driving situation, so that they existed mostly in the acceleration parts of the NEDC cycle. These particles were most likely soot mode particles. This is in line with the chemical composition results that show that, as the ethanol content of fuel increased, the rBC emissions decreased.

Figure 9 shows also that from viewpoint of particle number the role of cold start remained important also with the high ethanol

10   content fuels. In fact, most of the particulate emissions for E100 are related to the cold start situation. For E10, 37% of particle number was emitted during the first part of the cycle (CSUDC, 0-391s, see Karjalainen et al., 2016). While for E85 and E100 43% and 77 % of particle number were emitted during the CSUDC part. Although it seems that the mean particle diameter slightly decreased when the ethanol content of fuel increased, the larger soot mode particles existed in the exhaust with all fuels. However, the concentration of soot mode particles decreased significantly when the amount of ethanol in fuel was

15   increased. Fuel changes affected clearly also nanoparticle emissions; the emissions of nanoparticles decreased as the ethanol content of fuel increased. However, we note that the decrease was larger in larger particles than for nanoparticles. At the end of cycle (800–1000 s) two distinct peaks were seen for E100. Same peaks were seen in rBC time series (see Fig. S19 in Supplementary material).

20   The aerosol formation during cold start was clearly seen also in secondary aerosol concentrations. As the ethanol content increases, the size of particles during cold start as well as during the whole cycle decreases. As the ethanol content of fuel increased a clear increase in nanoparticles after the PAM chamber was observed. Because nanoparticle emissions were observed to decrease as the ethanol content of fuel in primary emissions, this observation indicates that small particles can form also in the PAM chamber e.g. via condensation on particles smaller than lower size limit of instruments used, or via

25   nucleation. We note that Figure 10 indicates that the average particle size in exhaust emissions decreased as the ethanol content increased. This will likely affect the efficiency of how these particles are detected with the SP-AMS since the collection efficiency of aerodynamic lens used in the SP-AMS sharply decreases in particle sizes below 30 nm. It should be taken into account that size distributions shown here are number size distributions, not mass size distributions.

4. Conclusions

30   Ethanol is used in fuels to decrease the CO_2 emissions of transportation and thus to reduce adverse climate effects of traffic. This study shows that the use of these fuels produces benefits also by decreasing exhaust PM concentrations and thus having

a positive influence on air quality. A decrease in PM was seen in both primary emissions and secondary aerosol formation potential of exhaust emitted by a modern flex-fuel DISI vehicle.

The composition of primary emissions was observed to change as the ethanol content of fuel increased. The relative contribution of BC in particulate matter decreased, whereas the contribution of organic particulate matter and inorganic ions increased. The organics to rBC –ratios for the primary emissions of E10, E85 and E100 were 0.9, 2.1 and 3.1, respectively. For all fuels most of the particulate matter observed after the PAM chamber was consisting of organic compounds(E10; 89%, E85: 79%, E100: 61%). The organics to rBC –ratios measured after the PAM chamber the E10, E85 and E100 were 12, 8.3 and 3.1, respectively. The role of cold start was observed to dominate in secondary aerosol formation for E10 and E85. For E100 no significant increase in secondary aerosol concentrations due to the cold start was observed possibly because of the high OH reactivity of the sample suppressing the OH exposure. As ethanol content of fuel increased, secondary aerosol formation was observed to decrease significantly. For E10, the secondary aerosol formation was significantly larger than the primary PM emissions with secondary to primary PM –ratio of 13.4, whereas for E100 similar increase for PM mass after the PAM chamber was not observed. This can be caused e.g. by low SOA formation due to low OH exposure combined with losses in chamber e.g. due to wall losses and fragmentation due to high UV-intensities used in the chamber.

The large difference in the exhaust secondary aerosol formation between E10 and fuels with higher ethanol content can be explained by considering the emissions of potential aerosol precursors. The exhaust emissions for low-ethanol fuels contained less short-chained organic species (ethanol, formaldehyde, acetaldehyde, methane, ethene) than the exhaust for E85 and E100, but significantly more aromatic compounds (benzene, toluene, ethyl benzene, xylenes). Compounds with a low number of carbon atoms are unlikely to form secondary aerosol due to their high vapor pressure; conversely, aromatic compounds are considered the most important SOA precursors among anthropogenic hydrocarbons. Their major atmospheric sink is the reaction with the hydroxyl radical (Andino et al., 1996). It is also known that the SOA yields tend to decrease at high-NO_x concentrations (Henze et al., 2008). In our case, both the NO_x concentration and the aromatics concentration decreased when the fuel was changed from E10 to high-ethanol fuels, but the NO_x decrease was comparatively minor. At the same time, the concentration of OH-reactive, short-chained organic species increased. These factors together cause a strong decrease in the production of aromatic hydrocarbon oxidation products, which in turn decreases the production of secondary organic aerosol. The decrease in aromatic emissions may by itself be enough to explain the SOA reduction, but one should not omit the effect of the added reactivity presented by e.g. increased ethanol emissions, which may have an inhibiting effect by taking up a larger fraction of OH (similar to the inhibition caused by isoprene in the case of biogenic SOA formation, see Kiendler-Scharr et al. (2009)). The reduction in NO_x should in principle increase SOA formation, but the effect is minor compared to the inhibiting causes.

This study shows that the SP-AMS combined with the PAM chamber is an efficient tool to investigate the differences in the secondary aerosol formation potential between vehicle technologies (fuels) with a high-time resolution taking the driving

conditions into account. However, the study strongly recommends including a high time-resolution particle size distribution measurement parallel with the SP-AMS. In general, the information gathered in this study is important for legislative purposes as well as for modelers and city authorities building emission estimates.

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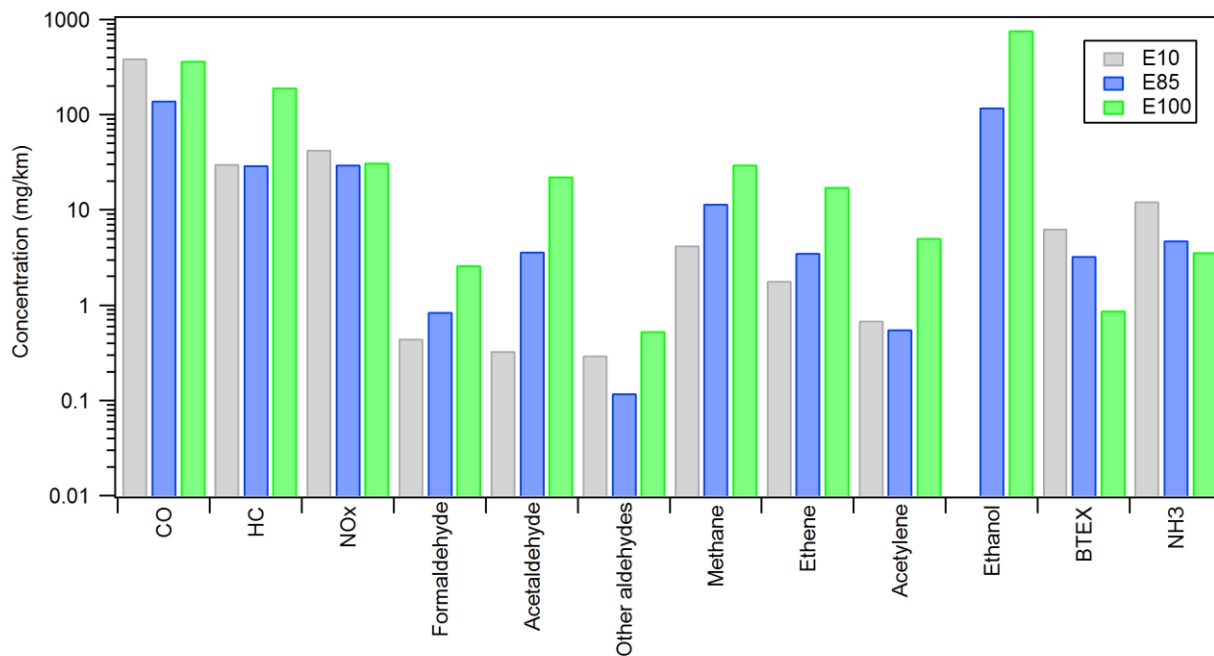
Figures:

Figure 1. Mean concentrations of gaseous compounds for different fuels measured during the NEDC cycle
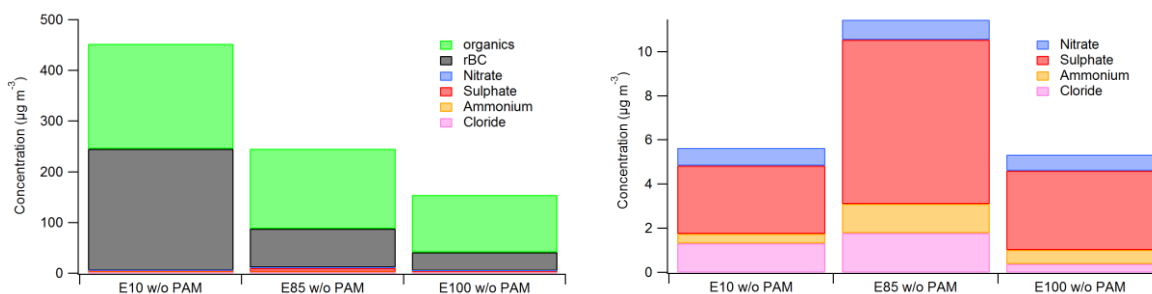
Figure 2. Chemical composition of primary particulate emissions for E10, E85 and E100 (left). Concentrations of inorganic ions(right).
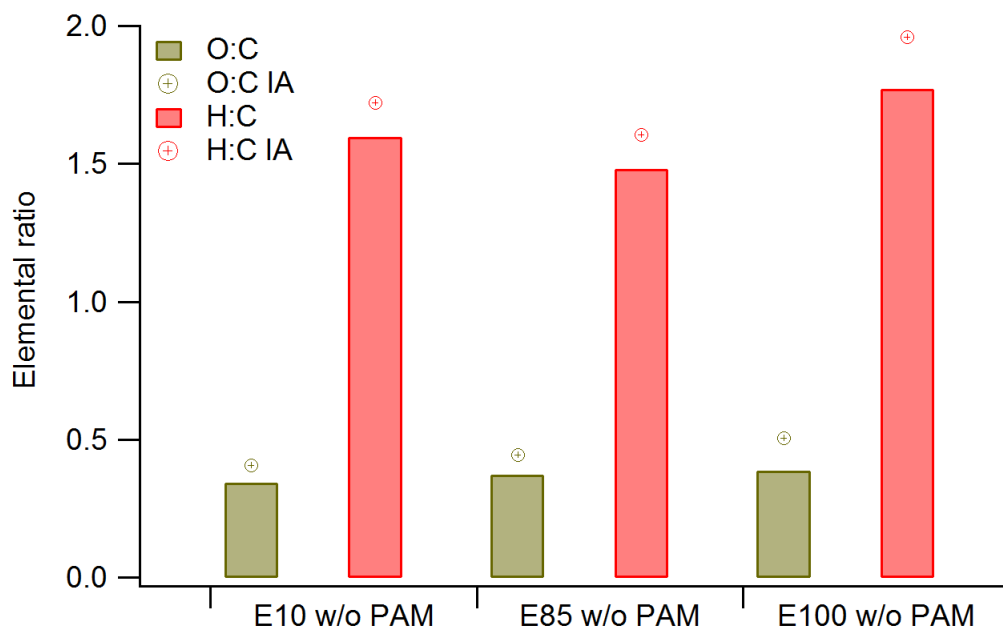
Figure 3. Average elemental composition (O:C and H:C ratios) of emitted primary PM during the NEDC cycle for E10, E85 and E100. Elemental composition is calculated using original method developed by Aiken et al. (2007) and using revised method (marked with IA=improved ambient) containing more atmospherically relevant organic compounds developed by Canagaratna et al. (2015).
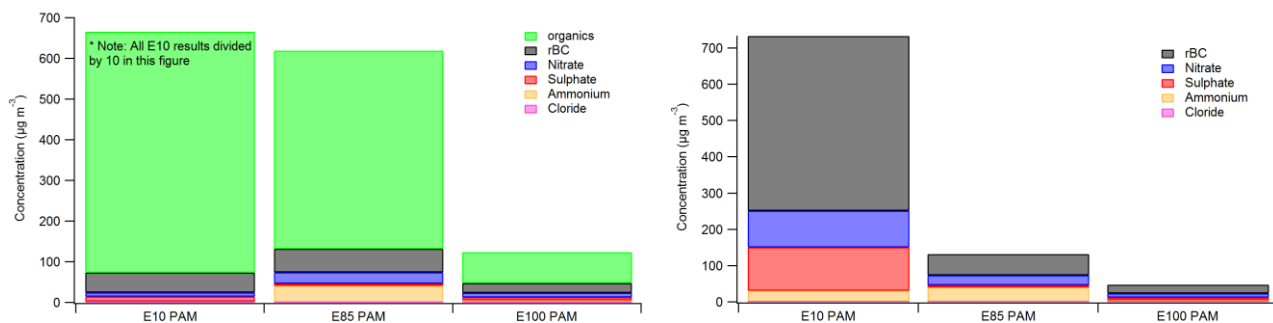
Figure 4. Composition of particulate emissions after the PAM chamber for E10, E85 and E100 (left; Note: in left figure all E10 results are divided by 10 in order to show all results in a same y-axis). Concentration of inorganic ions and BC after PAM chamber for E10, E85, E100 (right).
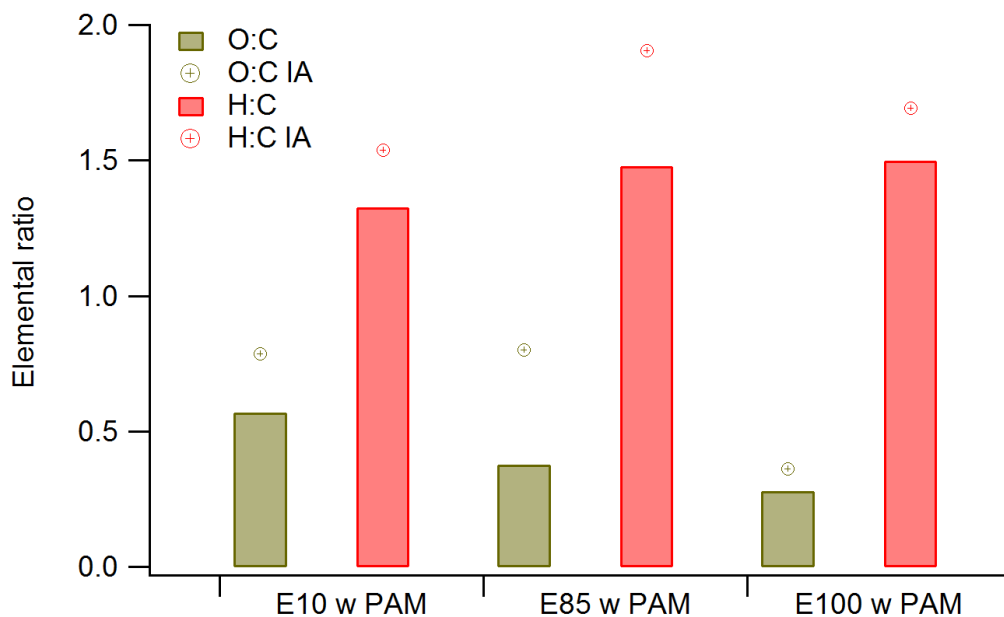
Figure 5. Average elemental composition (O:C, H:C) of formed secondary PM during the NEDC cycle. Elemental composition is calculated using original method developed by Aiken et al., (2007) and using revised method containing more atmospherically relevant organic compounds developed by Canagaratna et al., (2015) (marked with IA=improved ambient).
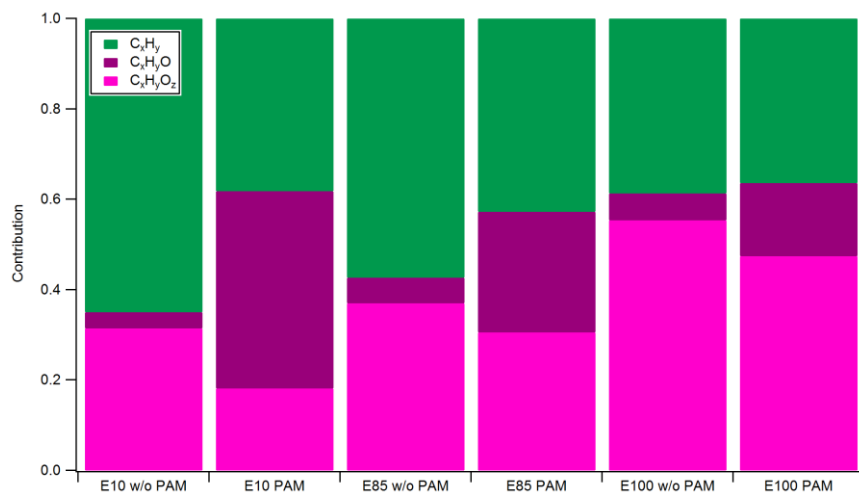
Figure 6. Contribution of different organic fragments with and without PAM chamber. CH refers to hydrocarbons (C_xH_y); CHO to fragments with one oxygen atom ($C_xH_yO_z^+$) and CHO$_x$ to compounds containing several oxygen atoms ($C_xH_yO_z$, z>1).
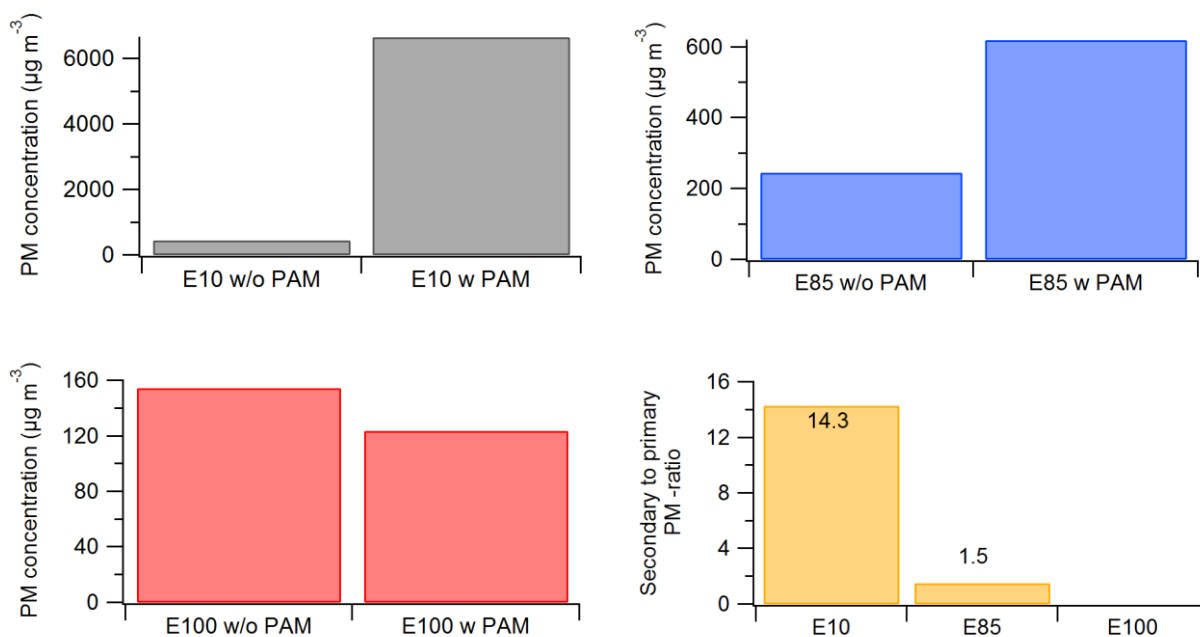
Figure 7. Primary submicron PM concentrations in exhaust emissions measured without PAM chamber and submicron PM concentrations measured with PAM chamber for E10 (a), E85 (b) and E100 (c). The secondary to primary PM –ratio for submicron PM mass in the exhaust calculated from the SP-AMS measurements (d). Concentration of secondary particulate emission was calculated by subtracting the concentration of primary PM from the PM measured after the PAM chamber.
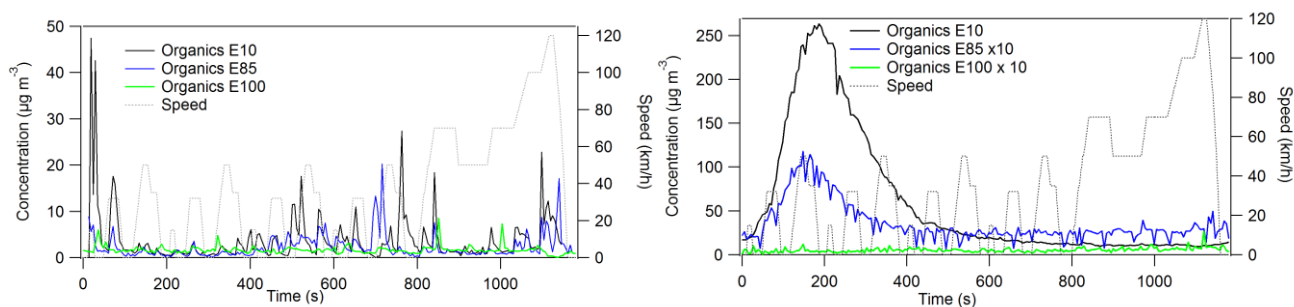
Figure 8. Time series of organic compounds for the primary emissions (a) and for the emissions measured after the PAM chamber (b). The speed profile of the NEDC is also shown.
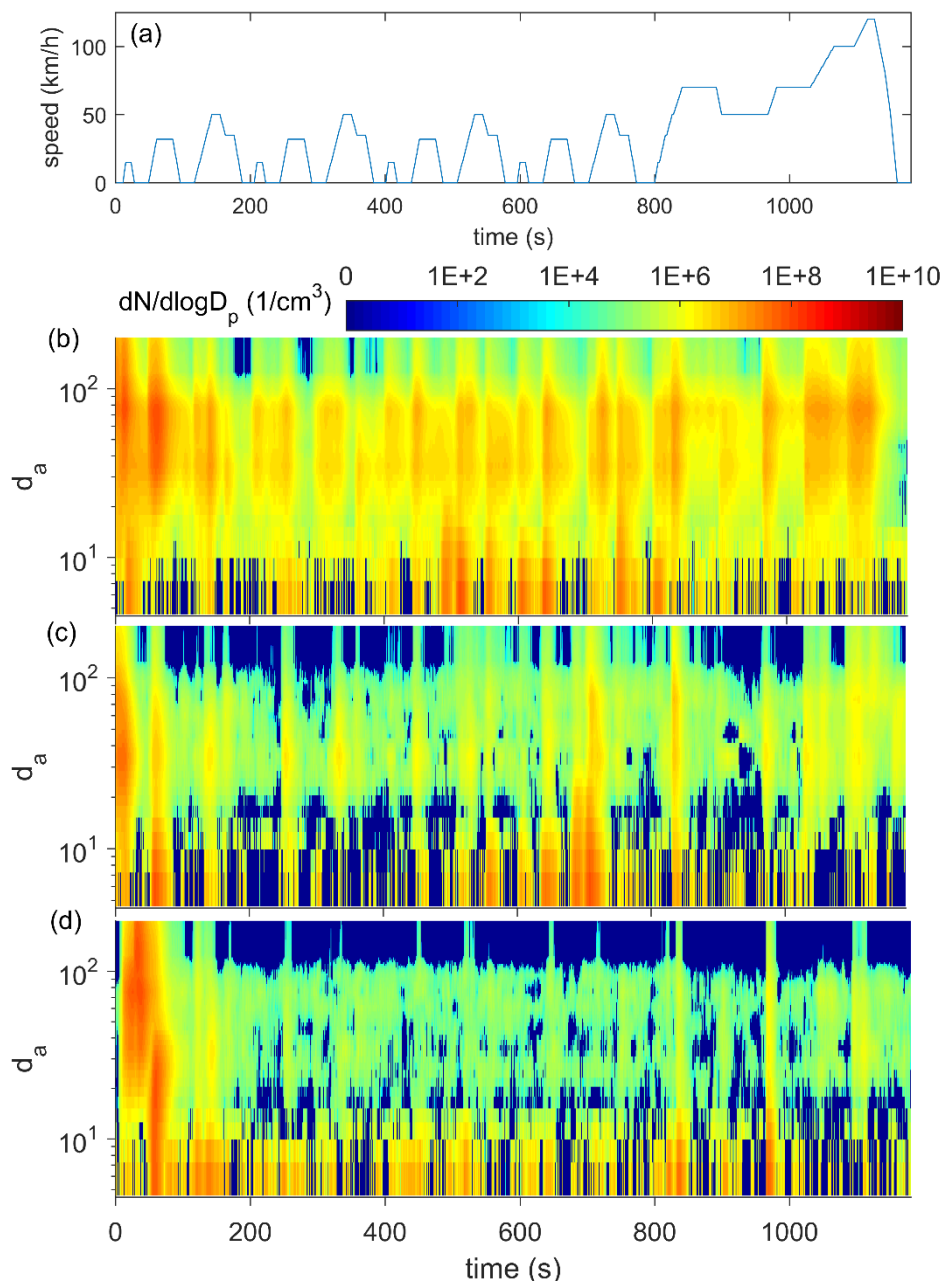
Figure 9. Number size distributions for primary particle emissions. Measurements were made during the driving cycle for all tested fuels, E10 (b), E85 (c) and E100 (d). The driving cycle (NEDC) is shown in the panel a.
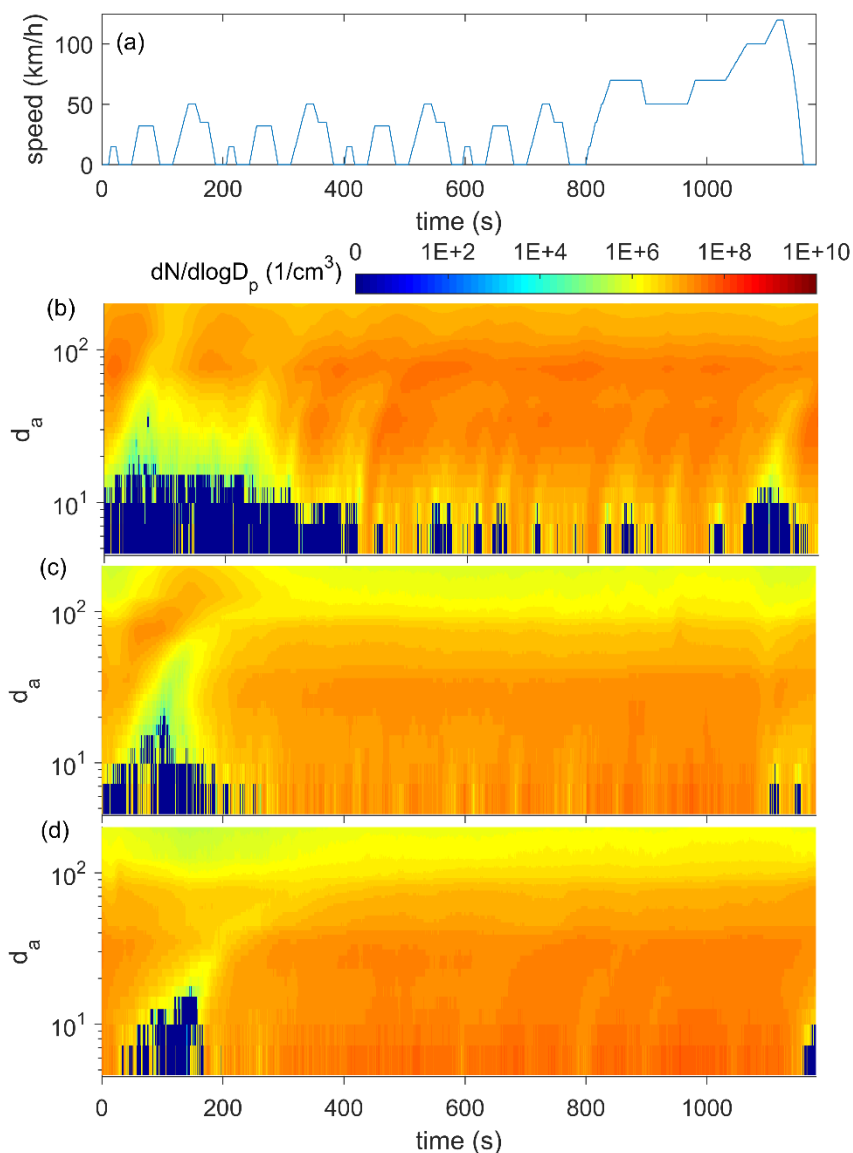
Figure 10. Number size distributions for the secondary particle emissions measured after the exhaust treatment by the PAM. Measurements were made during the driving cycle for all tested fuels, E10 (b), E85 (c) and E100 (d). The driving cycle (NEDC) is shown in the panel (a).

Tables:

Table 1. Average concentrations of main chemical compounds of PM (µg m^{-3}) during the NEDC cycle for primary (W/O PAM) and secondary (PAM) emissions.

CYCLE	ORG	NO$_3$	SO$_4$	NH$_4$	CHL	BC	TOTAL MASS
E10 W/O PAM	207.0	0.8	3.1	0.4	1.3	239.9	452.6
E10 PAM	5928.3	101.1	119.4	30.6	0.9	481.3	6661.7
E85 W/O PAM	157.3	0.9	7.4	1.3	1.8	76.7	245.4
E85 PAM	487.1	27.2	5.9	40.4	0.6	58.0	619.3
E100 W/O PAM	112.7	0.7	3.6	0.6	0.4	36.3	154.4
E100 W PAM	75.8	10.8	7.2	4.7	0.9	24.0	123.5