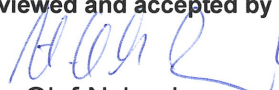


Research on Unregulated Pollutants Emissions of Vehicles Fuelled with Alcohol Alternative Fuels – VTT’s contribution to the IEA-AMF Annex 44

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Summary	
<p>IEA AMF project "Research on Unregulated Pollutants Emissions of Vehicles Fuelled with Alcohol Alternative Fuels, Annex 44" is a collaboration project between China, Canada, Finland, Sweden, Israel and Switzerland. Operating Agent of project is China Automotive Technology and Research Center (CATARC). Finnish contribution in Annex 44 covers tests with two FFV cars, representing MPI and DISI technologies, at two temperatures (+23 °C and -7 °C) by using E10 and E85 fuels. The third fuel, E100, was tested only at +23 °C. E85 reduced CO, but increased the HC emission when compared with E10. The dominating hydrocarbons present were methane, ethene, xylenes and acetylene for E85, whereas aromatics, methane and ethene dominated for E10. High ethanol emission was seen for the E85 fuel at -7 °C. Formaldehyde and acetaldehyde emissions were higher for E85 than for E10 in the beginning of the cold-start NEDC test. For E100, both cars experienced serious starting and driveability problems in the beginning of test at +23 °C, but not with warmed-up engine. Some of the emission phenomena observed were not fuel related. Firstly, the effect of test temperature was evident for the most emission species. NO_x emission, which was relatively low over the cold-start European test, was surprisingly high over the hot start test, particularly after a 10 minutes pause. This may indicate adjustments of an engine towards low CO and HC emissions at cost of increased NO_x in hot-start and heavy driving running conditions. In general, ammonia emissions were notable for the cars tested.</p>	
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Preface

“Research on Unregulated Pollutants Emissions of Vehicles Fuelled with Alcohol Alternative Fuels”, Annex 44, was carried out within the IEA’s Implementing Agreement on the Advanced Motor Fuels (AMF). Operating Agent of Annex 44 is China Automotive Technology and Research Center (CATARC). China, Canada, Finland, Sweden, Israel and Switzerland contributed with work to the project. Contributions in the form of cost sharing were received from the China, Sweden and Finland. The goal of Annex 44 is defined as follows: “...*the main purpose of this project is to obtain the unregulated pollutant emission levels of alcohols fuelled vehicles and gradually establish the measurement methods and standards limits of unregulated pollutants emissions. Furthermore, the influences of measurement methods, automotive technology, alcohol content in the fuel, ambient temperature, test cycles and other factors on the vehicle unregulated pollutant emissions will be researched.*” as presented in the description of Annex 44 in the IEA AMF website (www.iea-amf.org).

Activities of the total project are described by the Operating Agent of project, CATARC, at the IEA-AMF website (www.iea-amf.org). These cover, amongst other, *literature survey, comparative analysis of different measurement methods of the unregulated emissions, and effects of different vehicles and alcohol containing fuels on the unregulated emissions.* CATARC will compile the summary report of project. This report describes Finnish contribution to Annex 44.

Finnish contribution in Annex 44 covered emission investigation with two cars, three fuels, two temperatures and two test cycles. The responsible partner in Finland was the VTT Technical Research Centre of Finland. Work was carried out in cooperation with the Tampere University of Technology (TUT) and the Finnish Meteorological Institute (FMI) to gain in-depth understanding of nanoparticle formation and of secondary organic aerosols. TUT and FMI contributions belong to a parallel national project. Results obtained by TUT and FMI will be reported in scientific journals.

We acknowledge CATARC and partners of Annex 44, as well as the IEA AMF Executive Committee, for a possibility to contribute in this interesting project. Financial support from Tekes in Finland is acknowledged. Invaluable efforts of personnel involved in the measurements are gratefully acknowledged.

Espoo, 9 September 2014

Authors

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Abbreviations

AMF	The IEA's Implementing Agreement on Advanced Motor Fuels
CI	Compression Ignition (Diesel)
CO ₂	Carbon dioxide
CO	Carbon monoxide
CPC	Condensation Particle Counter
DISI	Direct-injection spark ignition
E85	Fuel consisting of ethanol close to 85 vol-% and gasoline-range hydrocarbons
ELPI	Electric Low Pressure Impactor
EUDC	The extra-urban driving cycle
FFV	Flexible-fuel vehicles
FMPS	Fast Mobility Particle Sizer
FTIR	Fourier transformation infrared
HC	Hydrocarbons
IEA	International Energy Agency
IOF	Insoluble Organic Fraction
MPFI	Multipoint fuel injection
MSAT	Mobile Source Air Toxic
NEDC	European exhaust emissions driving cycle; defined in the UN ECE R83
NH ₃	Ammonia
NO	Nitrogen oxide
NO ₂	Nitrogen dioxide
N ₂ O	Nitrous oxide
NO _x	Nitrogen oxides (NO and NO ₂)
OFP	Ozone forming potential
PAH	Polycyclic Aromatic Hydrocarbons
PAM	Potential Aerosol Mass chamber
PAN	Peroxyacetyl nitrate
PM	Particulate matter
PN	Particle number
SCR	Selective Catalytic Reduction
SI	Spark-ignition engine (Otto)
SMPS	Scanning Mobility Particle Sizer
SOA	Secondary organic aerosols
TWC	Three-way catalyst
VOC	Volatile organic compounds
WTW	Well-to-Wheel

1. Introduction

“Research on Unregulated Pollutants Emissions of Vehicles Fuelled with Alcohol Alternative Fuels, Annex 44” of the IEA’s Implementing Agreement on Advanced Motor Fuels (AMF), is presented by Operating Agent, CATARC, at the IEA AMF website (www.iea-amf.com). In this Chapter some background in emissions perspective is given.

High-oxygen-containing fuels, for example up to 85% ethanol (E85), can be used in special flexible-fuel vehicles (FFV). In Brazil, FFV cars are also designed for the use of hydrous E100 fuel. Methanol (M85) was used in the FFVs in early 90’s, and now it is used again, for example, in China. FFV cars are basically spark-ignition gasoline cars with some modifications. For example, all materials in the FFV cars are compatible with ethanol. Due to E85 fuel’s low energy content, fuel injectors of the FFV cars are designed for higher fuel flows than in conventional gasoline cars leading to higher volumetric fuel consumption despite of lower energy consumption. Feedback control in FFV cars adjusts fuel delivery and ignition timing. Ethanol’s higher octane rating would enable an increased compression ratio to achieve better energy efficiency. However, FFV cars still represent a compromise when compared to dedicated alcohol cars. The ignition of ethanol is poor, and therefore excess fuel is injected during cold starts when using E85 fuel to achieve performance similar to gasoline cars. Consequently, some exhaust emissions tend to be high when using E85 in the cold-start when the three-way catalyst is not warmed-up. Engine- and emissions-control technologies are expected to reduce cold-start exhaust emissions of the FFV cars using the E85 fuel in the future. (Lupescu 2009, Chiba et al. 2010, Kabasin et al. 2009, Yanowitz and McCormic 2009). Recently, a concern of adverse effect of ethanol on the aged TWC catalyst has been presented (Winkler et al. 2013).

When the automotive exhaust emissions are evaluated, it is important to consider harmfulness of the emissions. The US EPA’s Mobile Source Air Toxic (MSAT¹) list from 2007 discusses key MSATs: benzene, 1,3-butadiene, formaldehyde, acetaldehyde, acrolein, polycyclic organic matter (POM), naphthalene, diesel exhaust and gasoline particulate matter. Benzene, 1,3-butadiene, formaldehyde and benzo[a]pyrene have been classified as human carcinogens (IARC, 2010, 2012). Acetaldehyde (IARC, 1999) has been classified as a possible carcinogen. Many other compounds, such as PAHs and nitro-PAHs have been classified as proven, probable or possible carcinogens to humans. Ethene forms potential damages for plants and contribute in the formation of ozone and peroxyacetyl nitrate (PAN) (Gaffney and Marley 2011). Risk factors for calculating the cancer potency of exhaust gas are defined by many organisations. OEHHA (2009) defines cancer unit risks and potency factors for 107 carcinogenic substances or groups of substances. The US EPA IRIS (Integrated Risk Information System) is a human health-assessment programme that evaluates quantitative and qualitative risk information for effects that may result from exposure to environmental contaminants. The Nordic Swan labelling criteria for biofuels define substances, which are measured in accordance with a particular protocol, and calculate the cancer potency of exhaust gas using risk factors (Nordic Ecolabelling 2008). There are differences in the risk factors defined by different organizations.

Volatile organic compounds (VOC) contribute to the formation of ground-level ozone together with nitrogen oxides (NO_x) in the presence of heat and sunlight. Potential interactions between ozone and particulate matter emissions have been suggested. Precursor gases emitted by transport sources affect PM_{2.5}, PM₁₀ and ozone formation locally and in other regions. Exhaust and evaporative emissions from gasoline cars are the dominant source of VOCs within the transport sector, contributing 19% to the total VOCs emitted in 2010. Ozone causes adverse health effects, for example irritation of the respiratory system, coughing, throat irritation, reduction of lung function and induced asthma. There is also evidence of the

¹ US EPA (2007), 40 CFR Parts 59, 80, 85, and 86, Control of Hazardous Air Pollutants From Mobile Sources. Final Rule. 26 February 2007.

effect of ozone on, for example, cardiovascular related morbidity (US EPA 2007). Ozone contributes to damage to plants and ecosystems, which may lead to species shifts and losses reflecting also related goods and services (US EPA 2007). Individual VOC species contribute differently to formation of ozone and oxidants. Carter and Atkinson (1987) developed a maximum incremental reactivity (MIR) scale to assess the ozone-forming potential (OFP) of any emitted molecule. Environmental impacts can be analysed by various methodologies, such as CML2001 or ReCiPe2008, which take into account OFP, but also acidification potential (AP), photochemical oxidation creation potential (POCP), particulate matter formation potential (PMFP) and marine eutrophication potential (MEP) (Querini et al. 2011).

Transformation of primary exhaust emissions into secondary products is an important aspect when transport sector's emissions are assessed. For example, about 30% of PM₁₀ measured is in the form of secondary inorganic sulphate and nitrate aerosols, which are formed from the transformation of gaseous SO₂, NO_x and NH₃ emitted from various sources. These aerosols are presumably even more important as regards PM_{2.5} (EEA 2012a). Secondary organic aerosols are formed from atmospheric oxidation and subsequent condensation of various VOCs (EEA 2012a, AQEG 2005).

Ammonia originates mainly from agricultural sources. However, concern of traffic sources in the production of ammonium aerosols increased as the use of urea-based SCR systems for NO_x control for diesel vehicles became common. Ammonia is also formed by the three-way catalysts of the spark-ignited gasoline cars. Nitrous oxide (N₂O), a strong greenhouse gas, is also induced by catalyst chemistry under lean conditions. (Meijja-Centeno 2007, EEA 2012b).

The effect of E85 on the exhaust emissions

NO_x, CO and HC² emissions tend to be lower or at the same level for E85/FFVs than for gasoline at normal test temperature. NO_x comprises almost totally of NO while NO₂ emissions are low. Despite of low CO and HC emissions at normal test temperature, at -7 °C higher or similar emission level has been observed for E85 as for gasoline (Laurikko et al. 2013, Aakko et al. 2011, Yanowitz and McCormic 2009, Graham et al. 2008, Westerholm et al. 2008, De Serves 2005, Aakko and Nylund 2003). The latent heat of vaporization of ethanol is higher than that of gasoline leading to poor cold-startability and high emissions of organic gases at cold starts. (Chiba et al. 2010). On the other hand, fuel evaporative emissions are lower for E85 than for gasoline (Yanowitz and McCormic 2009, Westerholm 2008). Lower permeation emissions have also been reported for the E85 fuel than the non-ethanol fuel (Haskew and Liberty 2006, Kassel 2006, Stahl et al. 1992).

Higher *methane and ethene*, but lower *benzene, toluene and 1,3-butadiene* emissions are reported for E85 than for gasoline at normal temperature (Clairotte et al. 2013, Karavalakis et al. 2012, Yanowitz and McCormic 2009, Westerholm et al. 2008). At -7 °C, high methane, ethene, acetylene and BTEX emissions have been observed for the FFV car using the E85 fuel. (Aakko-Saksa et al. 2011).

The formaldehyde, acetaldehyde and ethanol emissions tend to increase substantially when E85 is compared with gasoline at cold starts at low temperatures (Clairotte 2013, Karavalakis et al. 2012, Aakko-Saksa et al. 2011, Yanowitz and McCormic 2009, Graham 2008, Westerholm et al. 2008 and De Serves 2005). Westerholm et al. (2008) reported that acetaldehyde emissions were 8–15 times higher for an FFV car using E85 than when using E5 at normal test temperature, and more than 100 times higher at a test temperature of -7 °C. Acetaldehyde, formaldehyde, and ethanol emissions represent a major part of organic gas emissions with ethanol containing fuels during the engine cold start (Chiba et al. 2010).

² A flame ionization detector (FID) takes into account all carbon-containing compounds. Therefore certain responses to oxygen containing organic gases are accounted (Sandström-Dahl et al. 2010 and Aakko-Saksa et al. 2011)

However, when engine and catalyst are warmed up, lower or similar acetaldehyde and ethanol emissions have been reported for E85 than for gasoline (De Serves 2005). Millet *et al.* (2012) reported that the increased ethanol use³ is estimated to elevate acetaldehyde concentration in atmosphere, which leads to higher PAN:NO_x ratio via peroxyacetyl radicals combined with lower NO_x emissions.

Particulate matter (PM) emissions for FFVs using E85 have been lower than for gasoline at normal temperature (Yanowitz and McCormic 2009). At -7 °C, higher PM emission has been observed for the E85 fuel than for gasoline, assumedly related to cold-start behaviour of car (Westerholm *et al.* 2008). Hayes *et al.* (2013) observed that elemental carbon emissions decreased with increasing ethanol content of fuel (Hays *et al.* 2013). For E85, low PAH emissions have been reported at normal test temperature, but elevated PAH emissions and cancer potency at -7 °C (Westerholm *et al.* 2008, Aakko-Saksa *et al.* 2011).

Lower *particle number emissions* have been observed for E85 than for gasoline at normal temperature, but the opposite has been seen at -7 °C (Westerholm *et al.* 2008, De Serves 2005). According to Lee *et al.* (2009), particle number emission decreased by 37% when E85 was compared with gasoline. In these studies, only dry particles were measured with so called “PMP” procedure. Szybist *et al.* (2011) concluded that low particle number emissions for E85 would enable using efficient direct-injection technology without penalty of high particle emissions.

Lower OFP for E85 has been reported when compared with gasoline at normal temperature (Graham *et al.* 2008). At cold temperature E85 may induce higher OFP due to increased ethanol, ethene and acetaldehyde emissions (Clairotte *et al.* 2013, Aakko-Saksa *et al.* 2011). These studies did not take into account atmospheric chemistry or the NO_x emissions. In the US, E85 has been estimated to slightly increase ozone under summer, but particularly over winter conditions. (Jacobson 2007, Ginnebaugh and Jacobson 2012). Negligible changes or varying results in OFP and PM have been reported for the dedicated E85 vehicles in the U.S. (Nopmongcol *et al.* 2011, Alhajeri *et al.* 2012). Formation of ozone is a complex process involving CO, VOC, NO_x and meteorological conditions, and it is not straight-forward to conclude the impact of fuel. (Querini *et al.* 2011).

Fridell *et al.* (2014) estimated that for regions in Sweden health risks decrease with E85 compared with gasoline due to decreased NO_x in relation to smaller effects on ozone, acetaldehyde, PM_{2.5} and benzene. However, authors pointed out that NO_x indicator may not be applicable for the E85 case, because there are differences in exhaust components associated with NO_x from different combustion processes.

Well-to-Wheel (WTW) environmental impacts of cars and fuels were analysed by Querini *et al.* (2011). Differences in emission impacts between fuels (E85, gasoline) were less significant than between car generations from Euro 3 to Euro 5. Also in the scenarios by Winther *et al.* (2012) emission impacts of E85 on NO_x, VOC and CO were small. These conclusions were based on the car emissions at normal temperature. According to Huo *et al.* (2009), E85 reduces VOCs, NO_x, PM and CO emissions in the life-cycle perspective in urban areas by up to 30%, as the major part of emissions are released in production of ethanol. Yang *et al.* (2012) claim that E85 does not necessarily outperform gasoline when wide spectrum of life-cycle environmental impacts is considered.

Ammonia (NH₃) or nitrous oxide (N₂O) are not directly fuel-related emissions. However, fuel has some indirect influence on these catalyst-generated emissions. Mejia-Centeno (2007) observed that low sulphur fuels reduce the formation of nitrous oxide emission while favouring the formation of ammonia. Clairotte *et al.* (2013) reported of lower ammonia emissions for E85 than for E5. Graham *et al.* (2008) observed that N₂O tends to increase

³ North America's ethanol emissions 670 Gg C/y in 2005.

with increasing ethanol content of fuel. In one study, nitrous oxide emissions were very low, mostly below 4 ppm, for three spark-ignition cars representing different engine technologies regardless of fuel. (Aakko-Saksa 2011)

2. Test matrix and methods

Work on Annex 44 in Finland was carried out in cooperation with VTT, the Tampere University of Technology (TUT) and the Finnish Meteorological Institute (FMI). VTT concentrated on the gaseous emissions, whereas TUT and FMI approached in-depth understanding on particle formation and on the secondary organic aerosols.

Test fuels comprised of a regular commercial E10 (max 10% ethanol), E85 (85% ethanol), and E100 (100% ethanol). E10 and E85 were available from the refuelling stations of St1 energy company. Anhydrous E100 was delivered by North European Oil Trade (NEOT) company in Finland. Deionized water was added into E100 to adjust water content to 4.4 %(m/m).

Two FFV cars were rented for the research project: Volkswagen Passat MultiFuel (DISI) and Ford Mondeo (MPFI), which are presented in Table 1.

Table 1. Test cars at VTT.

	FFV-DISI	FFV-MPI
Model year	2011	2010
Technology	1.4 litre turbo-charged DISI engine, 7 gear dual clutch autom. Transmission	2.0 litre natural aspirated MPI engine, 5 gear manual transmission
Weight	1557 kg	1477 kg
Odometer reading	48 700 km	43 600 km
Emission level	Euro 5	Euro 4

Cars were tested on a chassis dynamometer in a climatic test cell at +23 °C and -7 °C. The cold-start tests were carried out by using the European exhaust emissions driving cycle, “NEDC”, which is defined in the UN ECE R83 regulation (Figure 1). NEDC totals 11.0 km, divided into three test phases to study emissions at cold start and with warmed-up engines. The first and second test phases each consisted of 2.026 km driving, and the third test phase, the extra-urban driving cycle (EUDC), was 6.955 km.

In addition to “NEDC” test, also the hot-start test was applied to monitor how warmed-up cars performed. For this purpose, the FTP75 city driving cycle was run as a hot-start test, even though it is a cold-start test according to the definition by the US Environmental Protection Agency (EPA). FTP75 driving cycle totals 17.77 km, which is divided into three test phases including a 600 seconds pause (Figure 1).

Measurements were carried out over four weeks in September – October 2013. Daily sequence of tests with both cars was as follows:

- Cold-start European test “NEDC”
- “Dummy” test (FTP75) to stabilize cars for the actual hot-start test
- Hot-start FTP75 test

The first FTP75 test was run as a “dummy” to assure that cars were sufficiently warm, and to improve repeatability of tests. C1-C8 hydrocarbons and aldehydes were analysed only over the European NEDC driving cycle.

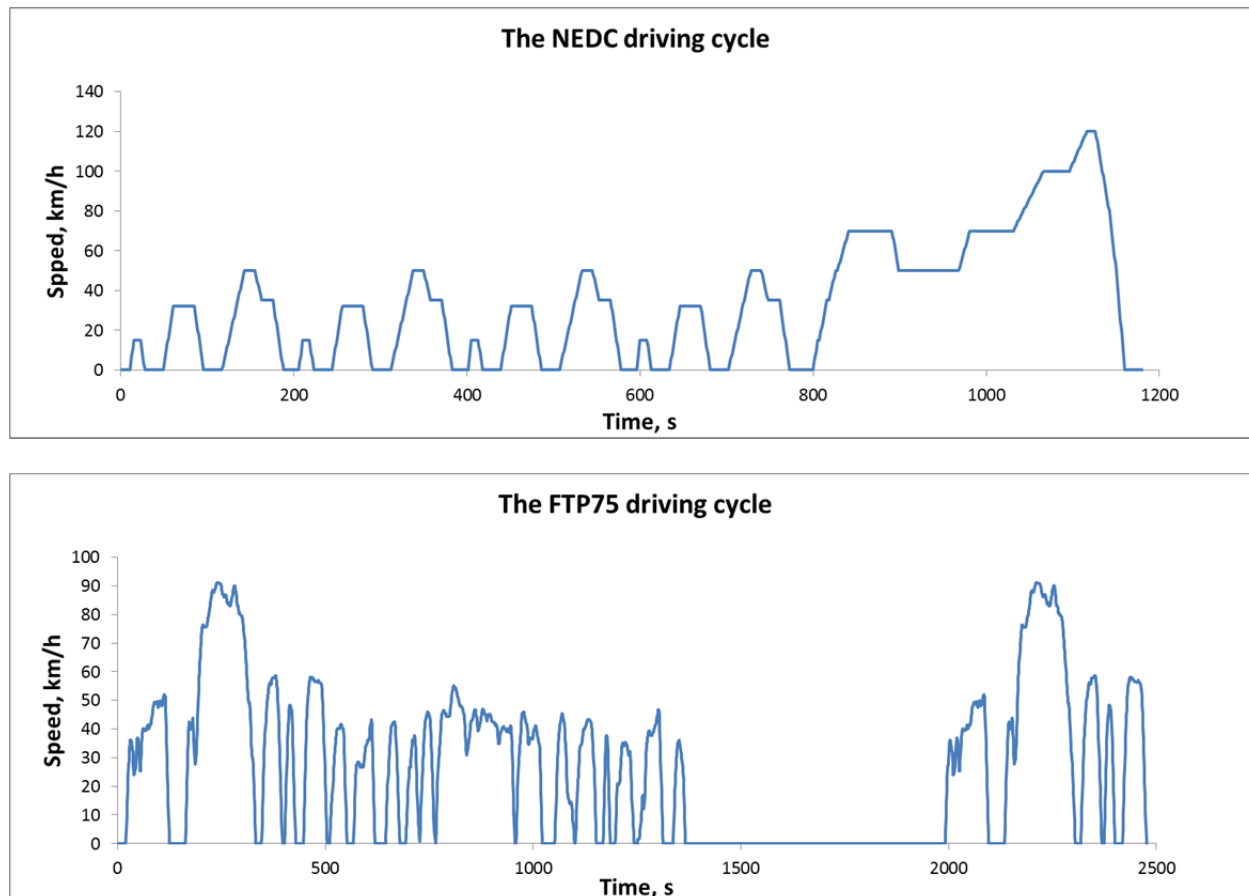


Figure 1. The NEDC and FTP75 driving cycles.

Test matrix is shown in Table 2. Finnish contribution covered emission investigation with two cars, three fuels (E10, E85, E100), two temperatures (+23, -7 °C) and two test cycles (NEDC, FTP). The E100 fuel was tested only at temperature of +23 °C, because the startability limit of neat ethanol is only around +12 °C.

Table 2. Test matrix at VTT. *) **)

	European test cycle			FTP hot-start test	
	E10 +23 and -7 °C	E85 +23 and -7 °C	E100* +23 °C	E10 +23 and -7 °C	E85 +23 and -7 °C
CO, HC, NO _x , CO ₂ , PM	2+2	2+2	2	2+2	2+2
C1-C8 hydrocarbons	2+2	2+2	2	-	-
Aldehydes	2+2	2+2	2	-	-
Multicomponent FTIR	2+2	2+2	2	2+2	2+2

*) The startability limit of neat ethanol is around +12 °C. Therefore E100 is not tested at -7 °C.

**) Additional steady-state tests were carried out for the particle characterization.

Gaseous regulated emissions. Equipment used in the measurement of the CO, HC, and NO_x emissions conforms to the specifications of the Directive 70/220/EEC and its amendments. The basic equipment are dynamometer Froude Consine 1.0 m, DC, 100 kW, constant volume sampler (CVS) AVL CVS i60 LD, Venturi-type and Pierburg AMA 2000, triple bench for gaseous regulated emissions. The true oxygen contents and densities of the fuels were used in the calculation of the results. A flame ionization detector (FID) used for measurement of hydrocarbons detects all carbon-containing compounds, also oxygenates (Sandström-Dahl et al. 2010). The calculation method chosen uses the density of 0.619 g/dm³ (different from the EC regulation 692/2008).

C1 to C8 hydrocarbons. The diluted exhaust gas for analysis of C1 to C8 hydrocarbons are collected from the same Tedlar bags that are used for measurement of the regulated emissions, and fed to the gas chromatograph, (HP 5890 Series II, AL2O₃, KCl/PLOT column, an external standard method). The hydrocarbons analysed are methane, ethane, ethene, propane, propene, acetylene, isobutene, 1,3-butadiene, benzene, toluene, ethyl benzene and m-, p- and o-xylenes. The detection limit is 0.02 mol-ppm, which corresponds to approximately 0.1 mg/km for methane, 0.5 mg/km for 1,3-butadiene and 0.7 mg/km for benzene.

Aldehydes are collected from the CVS diluted exhaust gas using 2,4-dinitrophenylhydrazine (DNPH) cartridges. The DNPH derivatives are extracted with an acetonitrile/water mixture and analysed using HPLC technology (Agilent 1260, UV detector, Nova-Pak C18 column). Aldehydes analysed are formaldehyde, acetaldehyde, acrolein, propionaldehyde, crotonaldehyde, methacrolein, butyraldehyde, benzaldehyde, valeraldehyde, m-tolualdehyde and hexanal. The detection limit for aldehydes corresponds to approximately 0.01 mg/km.

Multi-component analysis. A number of compounds were measured on-line using Fourier transformation infrared (FTIR) equipment (Gasmeter Cr-2000). More than 10 exhaust components from the raw exhaust gas were measured at two-second intervals. The concentrations of many compounds are low with gasoline-fuelled cars when compared to detection limits (Table 3). These detection limits were converted to corresponding mass-based emissions representing the duration of the European test cycle with certain assumptions.

Table 3. Detection limits determined from manufacturer's reference spectra at one-second intervals as concentrations and calculated mass emissions over the European test cycle (Aakko-Saksa et al. 2011).

	Detection limit	
	Concentration at 1-second intervals (ppm)	European test (mg/km)
Carbon monoxide (CO)	7	8
Nitric oxide (NO)	13	15
Nitrogen dioxide (NO ₂)	2/10	4
Nitrous oxide (N ₂ O)	4	4
Ammonia	2	1
Methane	2	1
Ethanol	4	7
Isobutanol	3	9
n-Butanol	4	12
ETBE	2	8
Formaldehyde	5	6
Acetaldehyde	5	9

Particulate matter. Particles were collected with an in-house designed high-capacity sampler (Kokko et al. 2000), which includes a dilution tunnel (Ø265 mm), a sample probe (Ø80 mm), two filter holders in parallel (Ø142 mm), a blower (Siemens ELMO-G, 2BH1 810-1HC36, 11 kW), a flow meter (Bronkhorst F-106C1-HD-V-12) and a controller (Stafsjö MV-E-80-P-TY-AC100-PN10). The sample flow can be controlled up to 2000 liters/minute to obtain appropriate particulate masses. In these measurements, a flow is 850–1200 litres/minute and two Ø142 mm filters are used in parallel. The filter type was Fluoropore 3.0 µm FSLW. A Sartorius SE2-F microbalance was used for weighing.

Real-time *particle number size distributions* by using Electrical Low Pressure Impactor (ELPI, >8 nm) equipment by VTT after the TUT's dilution system shown in Figure 3 to validate stability of the measurements and to screen tailpipe particle emissions. In Europe, a particle number limit applies to the Euro 5/6 emission level light-duty vehicles with certain exceptions. The procedure takes into account only solid "dry" particles as the volatile portion of particles is evaporated before the measurement. The particle number measurements with ELPI at VTT took into account total number of "wet" particles. Therefore the European PN limit of 5×10^{11} #/km is not relevant for the results of this report.

In-depth analyses of nanoparticle formation and of secondary organic aerosols were carried out by the Tampere University of Technology (TUT) and the Finnish Meteorological Institute (FMI). Primary (tailpipe) emissions go through atmospheric transformations leading to secondary emissions. FMI and TUT studied this phenomena by using the Potential Aerosol Mass (PAM) chamber to oxidize primary emissions into secondary organic aerosols (SOA). Measurements were carried out before and after the PAM chamber.

FMI characterized before and after PAM from sub-micron PM: organics, sulfate, nitrate, ammonium, chloride, black carbon and metals (e.g. Ni, V, Ba, Cr, Fe, etc) with time resolution of 5 seconds by using the SP-AMS equipment (Figure 2).



Figure 2. FMI characterized before and after PAM from sub-micron PM: organics, sulfate, nitrate, ammonium, chloride, black carbon and metals.

TUT focused on in-depth characterization of particles by on-line detection of particle number sizes and number concentrations as “particle maps”. In addition to primary particles, also secondary aerosol formed in atmospheric reactions is studied (after PAM chamber). TUT’s test set-up for exhaust dilution and measurements is shown in Figure 3. An example of “particle maps”, which will be analysed in the scientific articles, is presented in Figure 4.

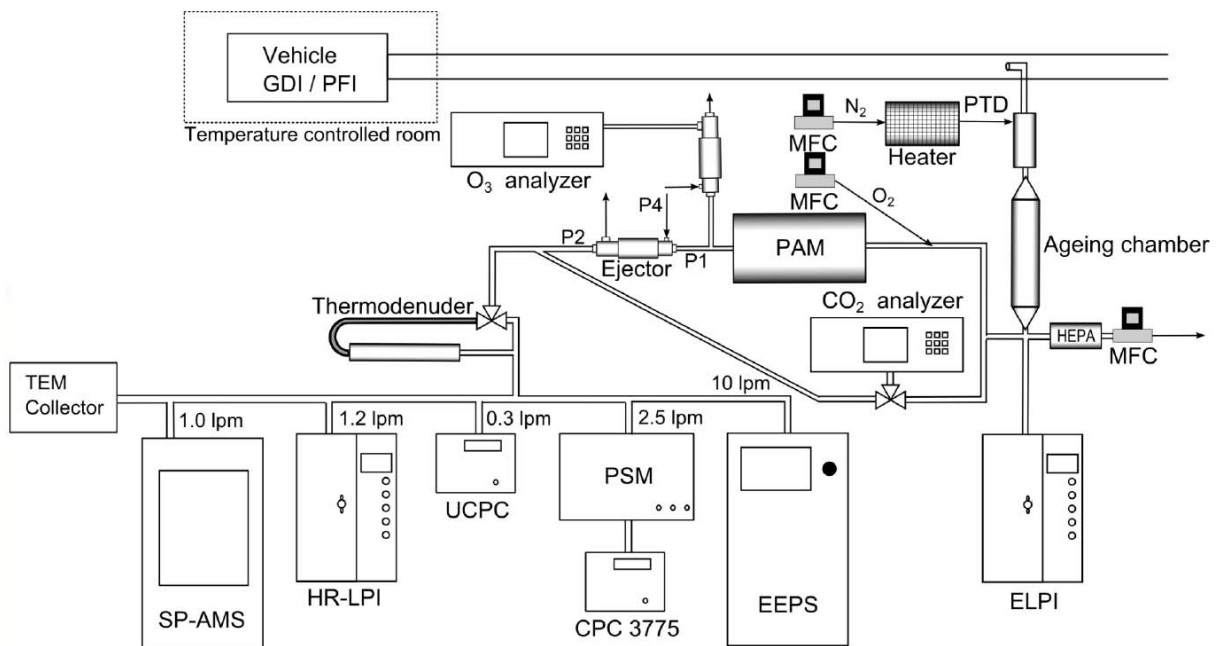


Figure 3. TUT test set-up for in-depth characterization of particles.

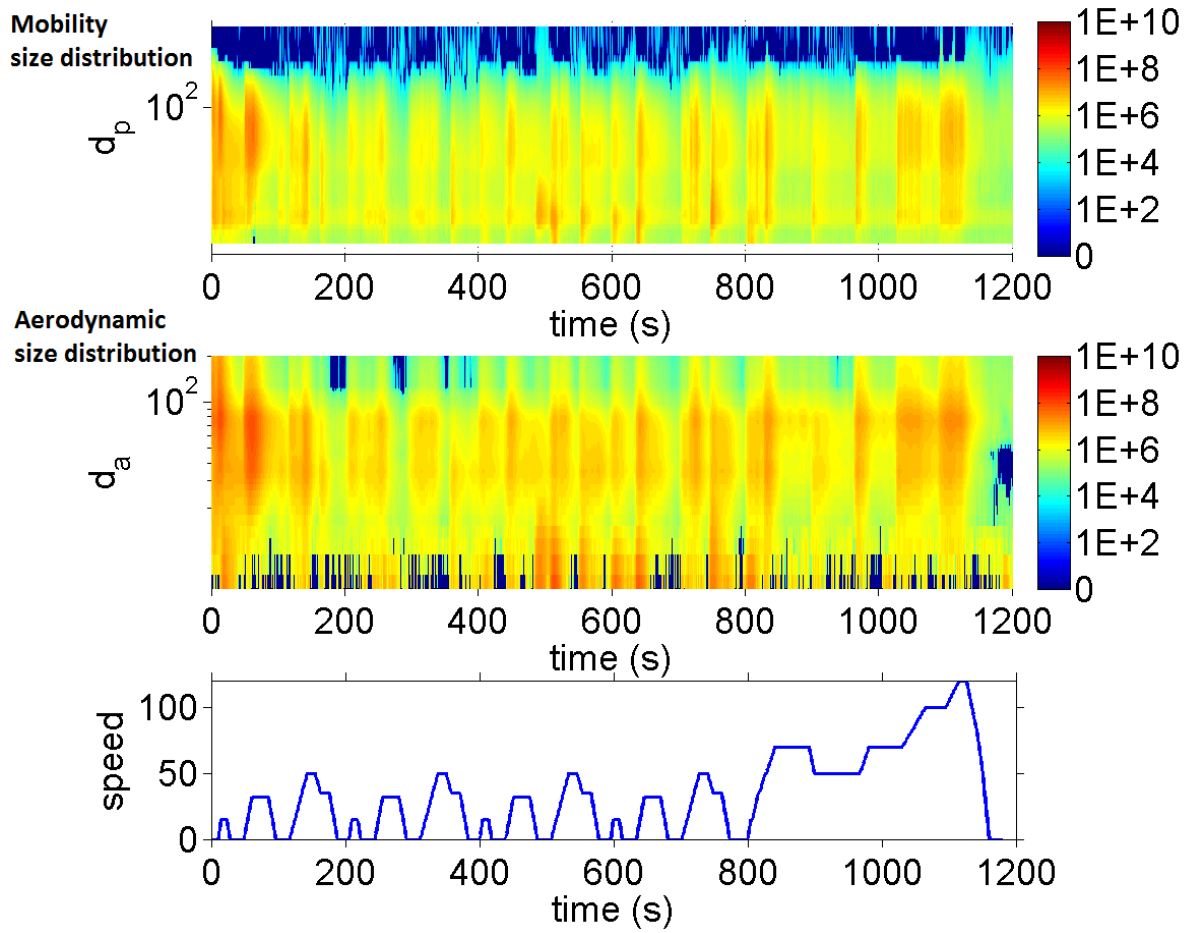


Figure 4. An example of “particle maps” from TUT measurements.

3. Results

3.1 CO and HC emissions

CO and HC emissions were higher at -7 °C than at +23 °C in the cold start NEDC test, particularly for the MPI car (Figure 5). Relatively low CO and HC emissions were seen over the hot start FTP75 test at both temperatures, though some differences were observed between cars. CO emission was higher for the MPI car than for the DISI car.

The CO emission was generally lower for E85 than for E10 with both cars, temperatures and test cycles. E100, however, showed similar or elevated CO emission when compared with E10 or E85 fuels at +23 °C.

HC emissions were elevated with the E85 and E100 fuels when compared to E10. Analysis method for total “HC” accounts carbonyl emissions in addition to hydrocarbons.

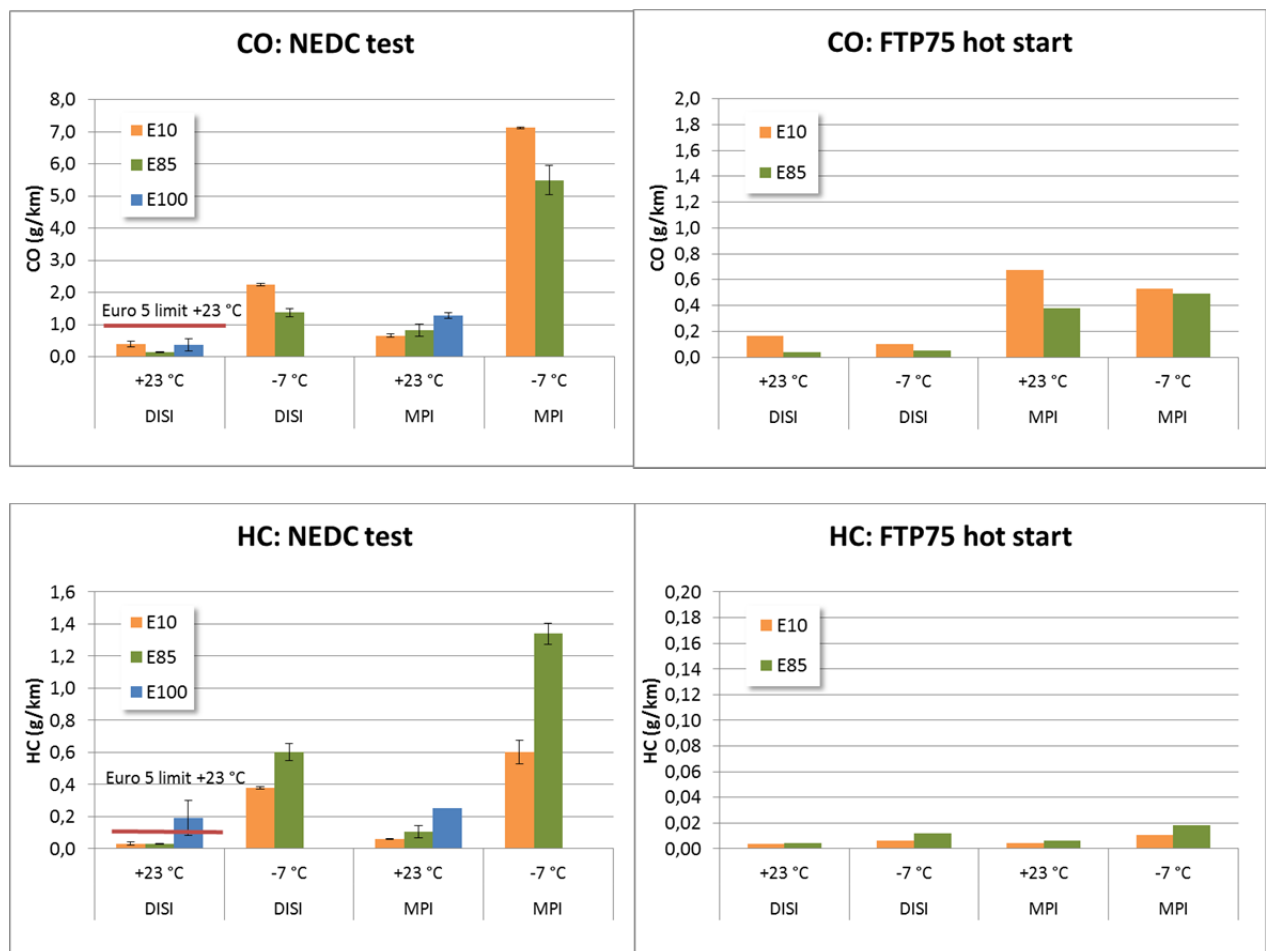


Figure 5. CO and HC emissions over cold-start NEDC and hot-start FTP75 test cycles.

Individual C1-C8 hydrocarbons were considerably higher at -7 °C than at +23 °C for both cars over the NEDC test cycle (Figure 6). Sum of C1-C8 emissions was generally higher for the MPI car than for the DISI car, particularly at -7 °C.

For E85 at +23 °C, the main C1-C8 compounds present were methane, and to lesser extent ethene, xylenes and acetylene. The overall C1-C8 emissions were higher for E100 than for E85 at +23 °C. For E10, the sum of C1-C8 emissions were at the same level as those for the

E85 fuel, but the composition was different. For E10 the predominant compounds observed were aromatics (toluene, xylenes), and to lesser extent ethene and methane.

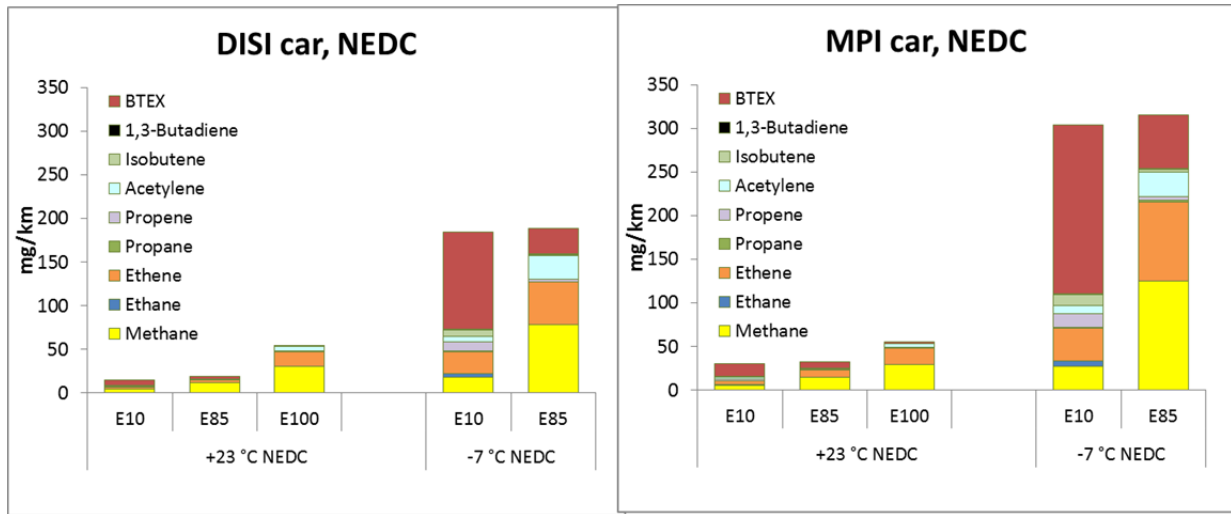


Figure 6. C1-C8 hydrocarbon emissions over the cold-start NEDC test.

3.2 Ethanol and aldehyde emissions

An overview of the selected unregulated emissions is shown in Figure 7. In the European test cycle aldehydes and speciated hydrocarbons were measured with HPLC and GC methods, whereas less accurate FTIR technology was used for these emission species in the FTP75 test cycle. Therefore an overview given in Figure 7 is indicative for the FTP75 tests. Alcohols were measured only by FTIR in all tests.

Alcohol emissions, primarily ethanol, dominated for the E85 and E100 fuels in the cold-start NEDC test. Particularly high ethanol emissions were seen in the NEDC test at -7 °C for the E85 fuel. An ethanol emission of 1.5 g/km over NEDC at -7 °C would mean that around 2.1% of E85 fuel consumption ends up as unburnt exhaust ethanol (assuming 70 g/km fuel consumption). For E100, ethanol emissions were substantial at +23 °C. It is noticeable that ethanol emissions were very low for E85 and E100 in the hot-start FTP75 test at both test temperatures.

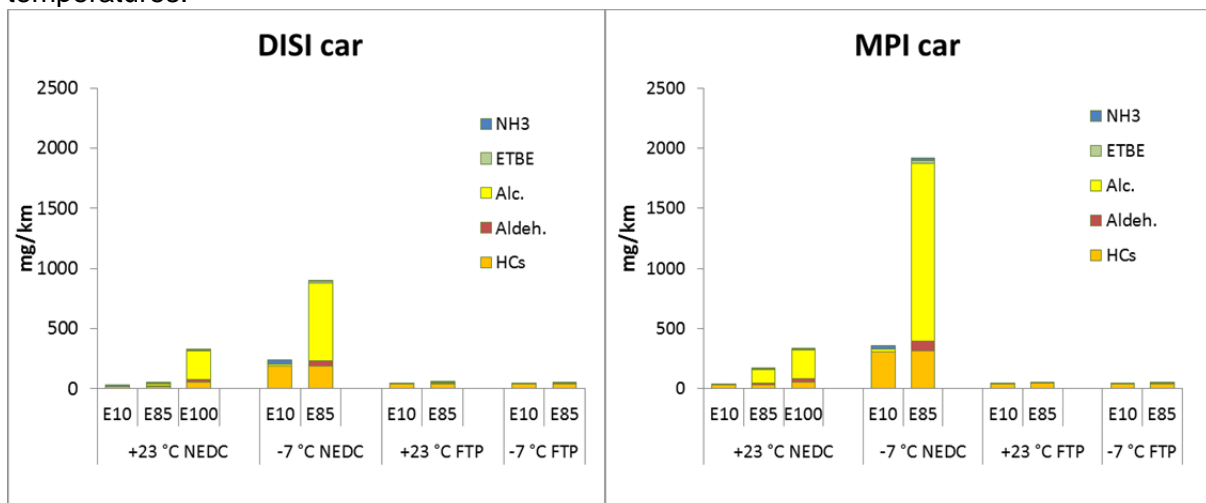


Figure 7. Overview of unregulated emissions over the cold-start NEDC test and hot-start FTP75 test.

Acetaldehyde is the second highest emission after ethanol emission for the E85 and E100 fuels. Acetaldehyde emissions increased dramatically with higher fuel ethanol content, particularly at low test temperature with the MPI car (Figure 8). Generally, formaldehyde and acetaldehyde emissions were higher for the E85 and E100 fuels than for the E10 fuel in the cold-start NEDC test. In the hot-start FTP75 test, aldehyde emissions were negligible for both cars and fuels.

Formaldehyde emissions from both cars measured were low even when the tightest formaldehyde limit of 4 mg/mi in California for SULEV cars is regarded. The formaldehyde emission was at the highest level for the DISI car when using E85 fuel at -7 °C, namely 4.5 mg/km.

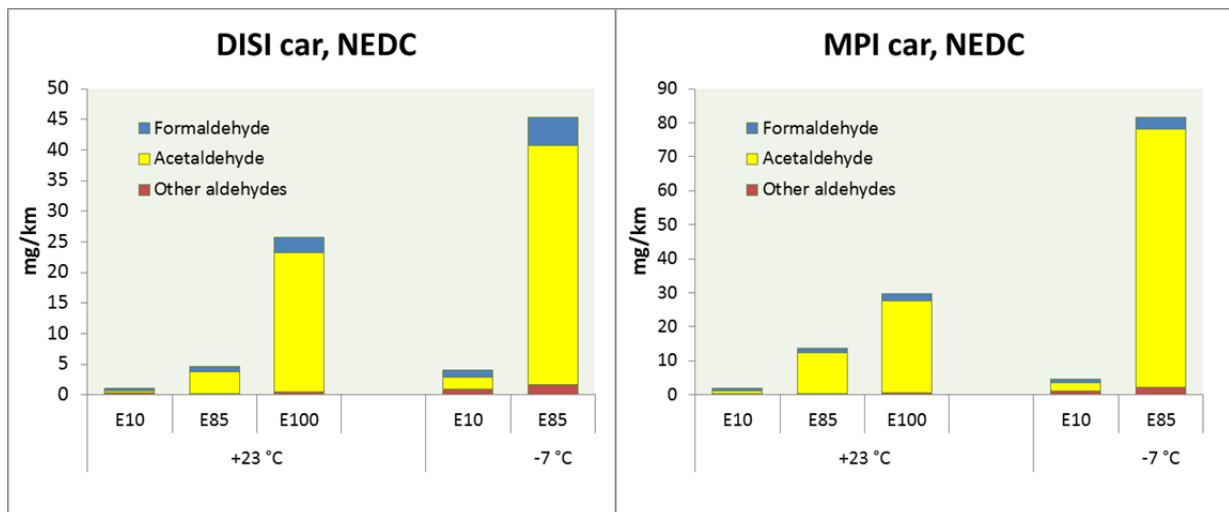


Figure 8. Formaldehyde and acetaldehyde emissions over the cold-start NEDC test.

Acetaldehyde emission was observed in substantial concentrations over 3 minutes after the cold-start of car at -7 °C (Figure 9). At +23 °C test temperature acetaldehyde emission peaked over much shorter period after the start of the car. Formaldehyde emission was seen in significant concentrations only in the beginning of the test.

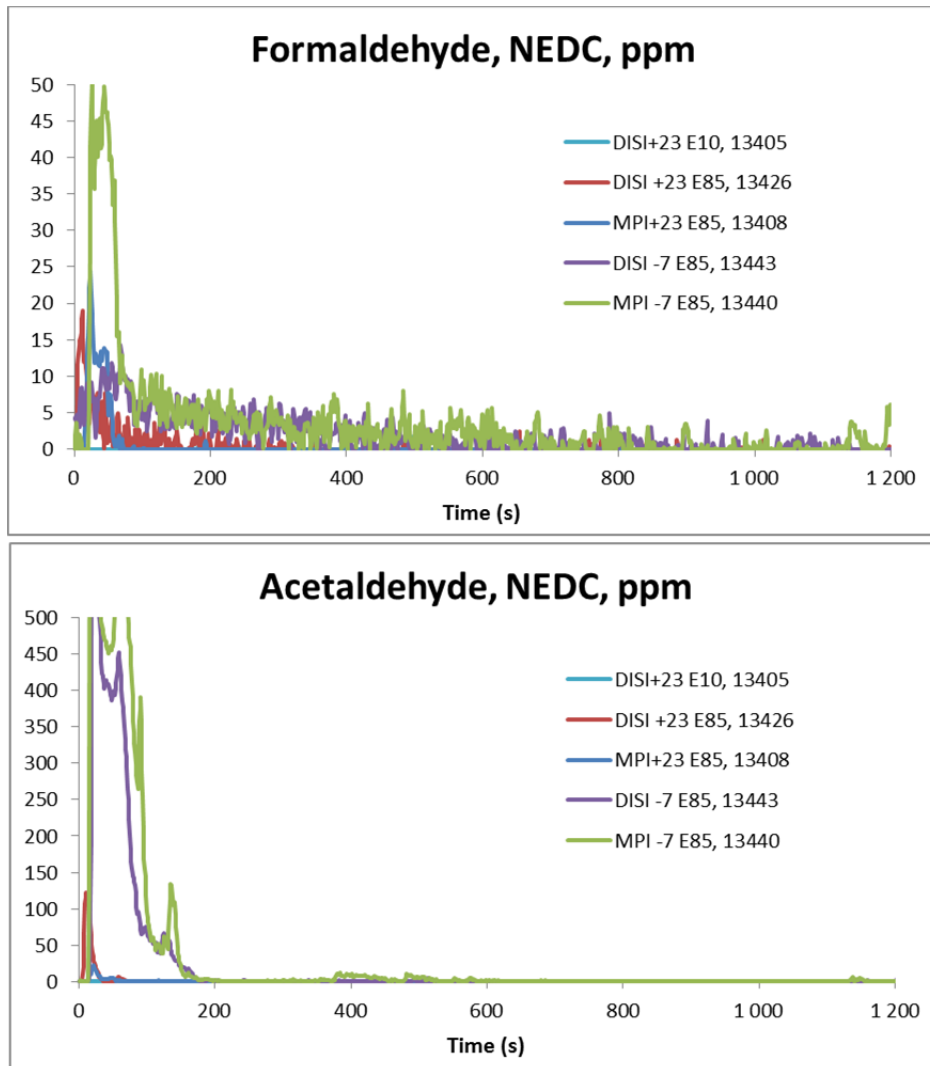


Figure 9. Formaldehyde and acetaldehyde emissions over the NEDC test.

3.3 NO_x , ammonia and nitrous oxide

The NO_x emissions were relatively low over the cold-start NEDC test, even though elevated emissions were observed for the DISI car at -7 °C (Figure 10). Only small differences in NO_x emissions between fuels were detected for the DISI car over the NEDC test. With the MPI car, slightly elevated NO_x emissions were observed for the E85 fuel, but not for the E100 fuel.

Over the hot start FTP75 test, the NO_x emission level was surprisingly high. NO_x emission for the MPI car with E85 was 228 mg/km at +23 °C and 139 mg/km at -7 °C. NO_x emission for the DISI car at -7 °C was up to 343 mg/km. High NO_x emissions were not expected in the hot-start test with warmed-up engine. In addition, higher NO_x emissions for the E85 fuel than for the E10 fuel was unexpected.

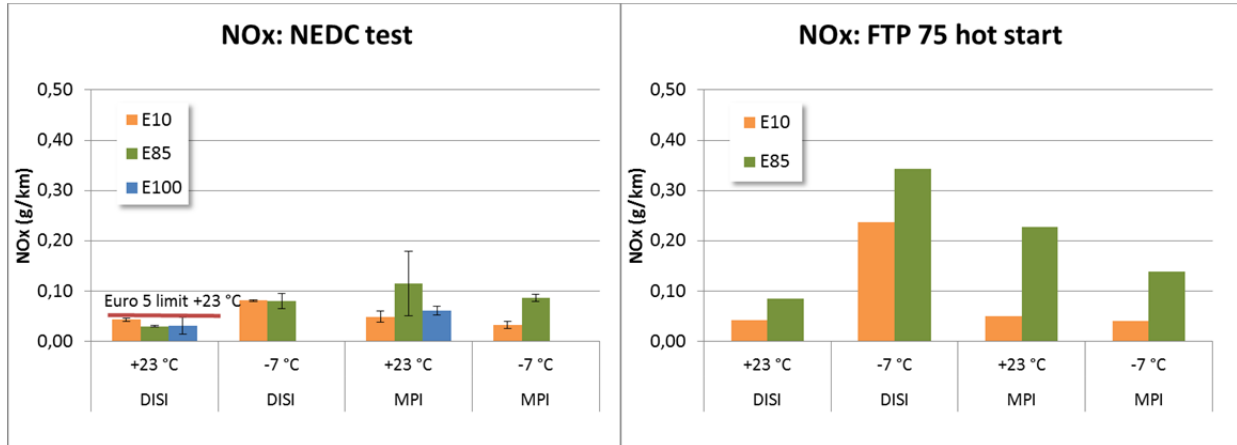


Figure 10. NO_x emission over cold-start NEDC and FTP75 test cycles.

Figure 11 shows NO_x concentration with DISI and MPI cars over the cold-start NEDC and hot-start FTP75 tests at -7 °C. In the NEDC test, NO_x was emitted in the beginning of test after the cold start and during accelerations. In the hot-start FTP test, high NO_x concentrations were observed in the accelerations, however, the highest emissions were seen after a 10 minutes pause. This indicates that these engines may be optimised for low CO and HC emissions leading to conditions that are not favourable for reduction of NO_x in the TWC due to possibly lean air-to-fuel ratio. Results in different test phases are shown in Appendix 3.

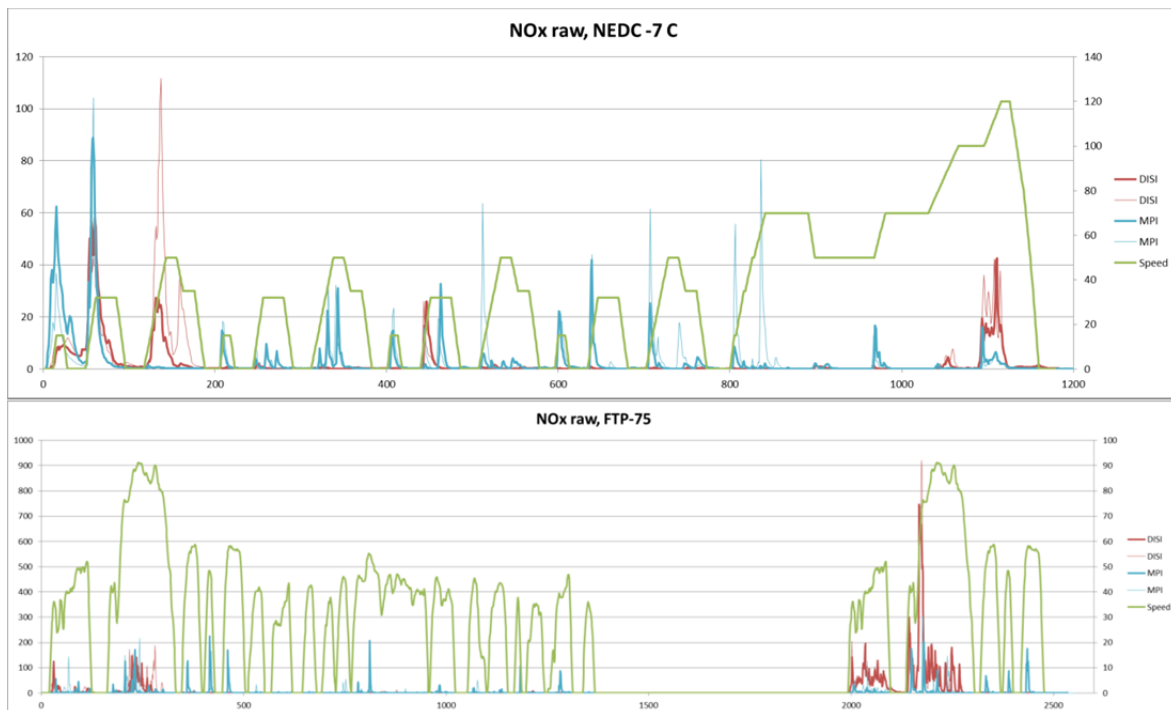


Figure 11. NO_x emissions in the NEDC and hot-start FTP test.

Ammonia, nitrous oxide and nitrogen dioxide emissions are shown in Figure 12. Nitrogen dioxide emissions were low, below 3 mg/km. Nitrous oxide emissions were also low, below 5 mg/km. Both of these emissions were practically below the detection limit of the FTIR method, whereas ammonia emission clearly exceeded the detection limit.

Ammonia emission was higher at -7 °C than at +23 °C in the cold-start NEDC test. The hot start FTP75 test at both temperatures showed similar level of ammonia emission as the

NEDC test at +23 °C. MPI and DISI cars emitted quite similar emission levels of ammonia. The highest single emission result, close to 50 mg/km, was obtained for the E10 fuel with the DISI car over the NEDC test cycle at -7 °C.

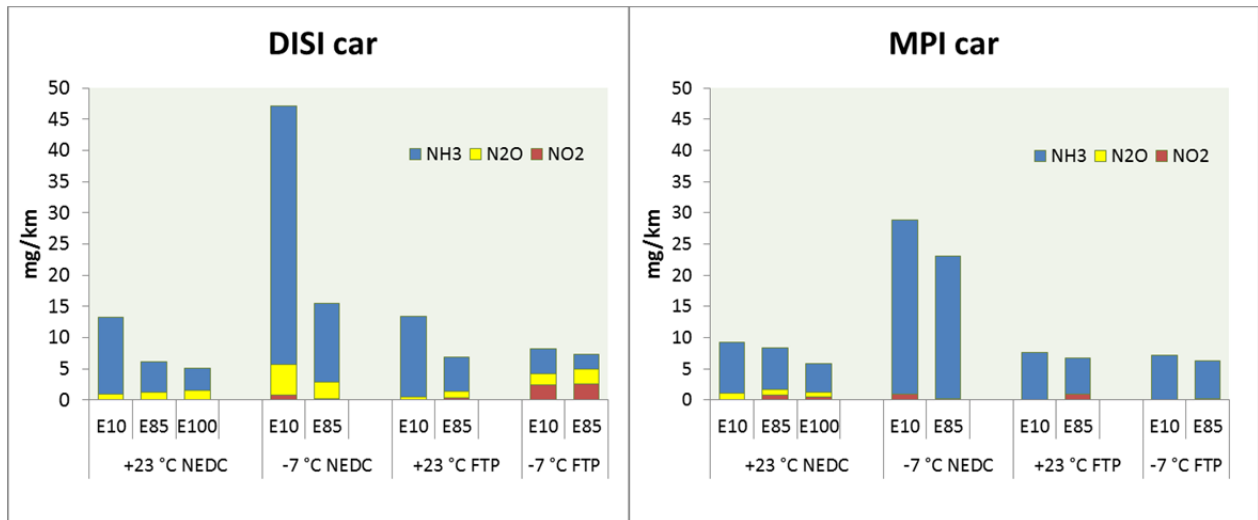


Figure 12. Ammonia, nitrous oxide and nitrogen dioxide emissions over the cold-start NEDC and hot-start FTP75 driving cycles.

Ammonia concentrations are presented in Figure 13. Ammonia concentrations were high in general, exceeding 10 ppm in major part of tests. In addition, substantial peaks up to 300-500 ppm were observed. These ammonia concentrations are high when compared to limit value of 10 ppm for SCR equipped heavy-duty engines, for example.

Ammonia concentrations in Figure 13 are not carefully adjusted with the test cycle, and therefore the test cycle dependence cannot be analysed. However, slight correlations between ammonia formation and the test cycle could be present. In theory, ammonia formation is enhanced in slightly rich air-to-fuel ratio at high temperatures (aggressive accelerations) when sufficiently HC and NO_x emissions are present (Li *et al.* 2010, Mejia-Centeno 2007, Heeb *et al.* 2006). Engine-out emissions were not measured in this project, but it is assumed that HC and NO_x are not a limiting condition for ammonia formation in these tests. The Pearson's correlation factors were calculated for emissions measured. However, reasonable explanations for ammonia formation were not found.

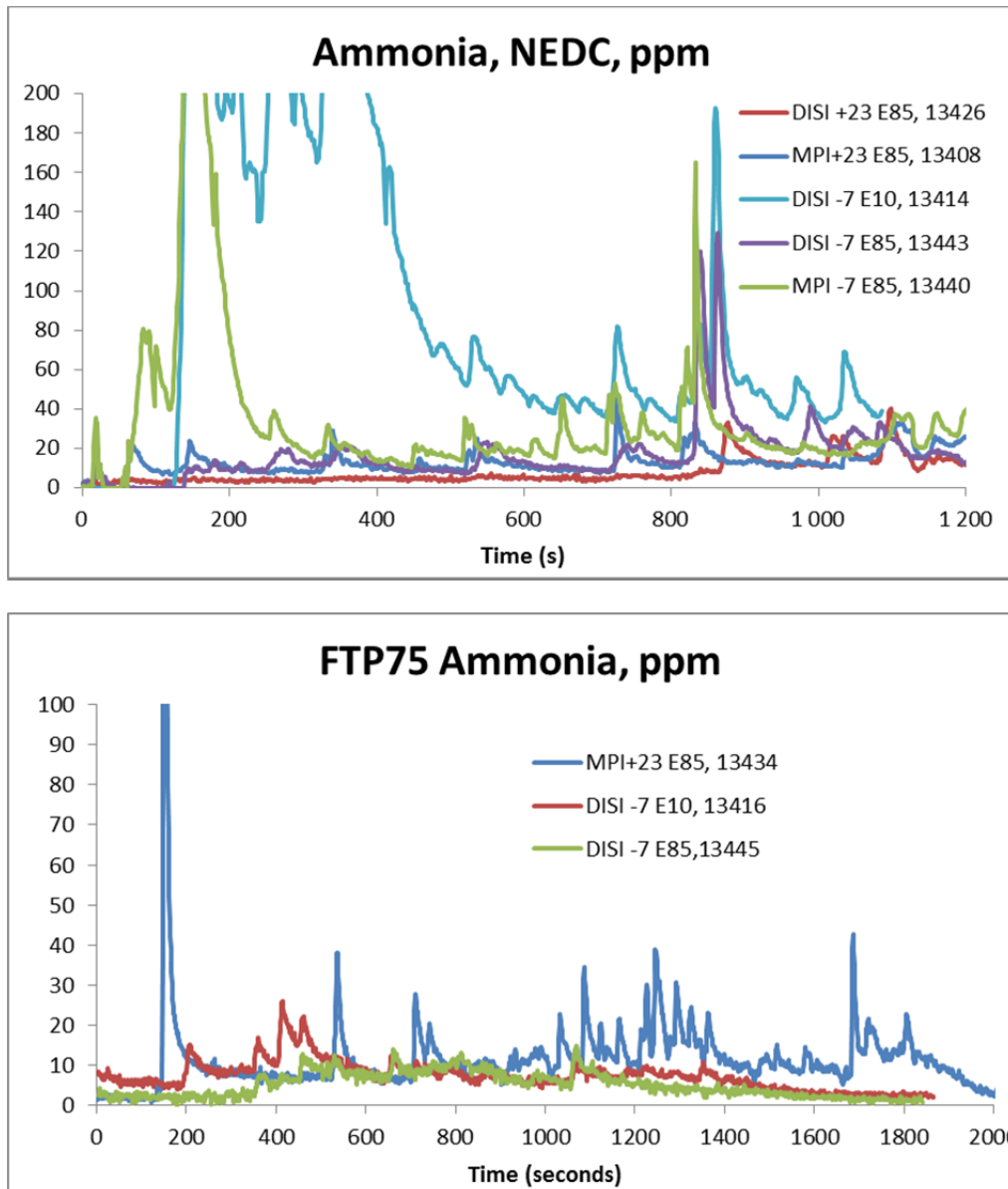


Figure 13. Ammonia concentrations over the selected tests.

3.4 Particle mass and number emissions

Particulate matter emissions (PM) were generally low (i.e. below 7 mg/km) in all cases, however, higher PM were observed at -7 °C than at +23 °C (Figure 14). By default, PM emissions decrease with increasing ethanol content of the fuel, and this was also the case in these tests. PM emissions were extremely low over the hot-start FTP75 test (below 1 mg/km) for both fuels and cars tested.

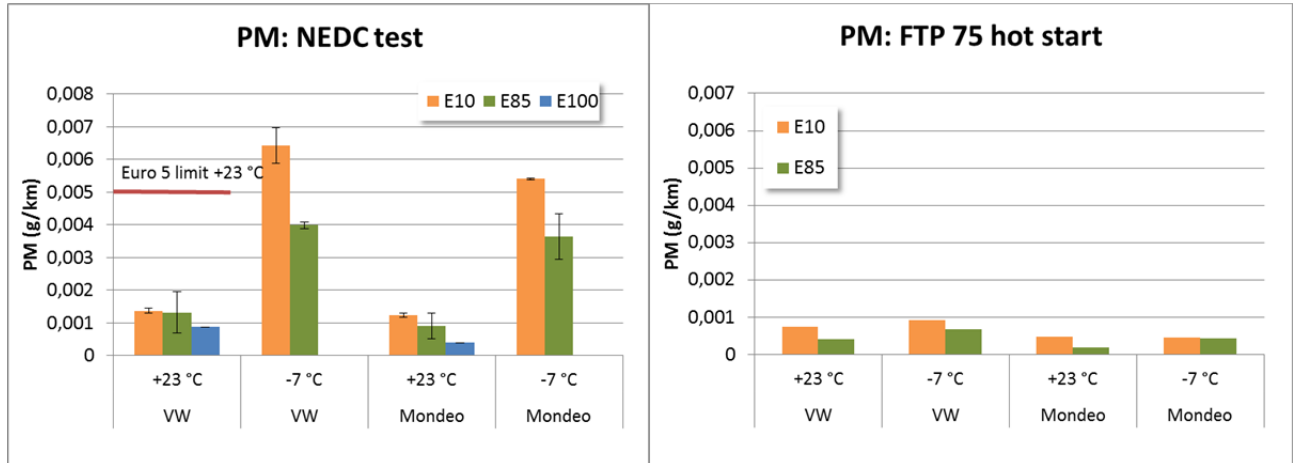


Figure 14. PM emission over the cold-start NEDC and the hot-start FTP75 driving cycles.

“Wet” particle number emissions (PN) were higher for E10 than for E85 over the NEDC test (Figure 16). So, E85 reduced particle number emissions effectively for both cars. PN results for E100 were extremely low. PN was relatively low for both cars over the hot-start FTP75 test. The “wet” particle number results here cannot be compared with the limit values of the the Euro 5/6 emission regulation, which takes into account only solid “dry” particles (volatile portion evaporated).

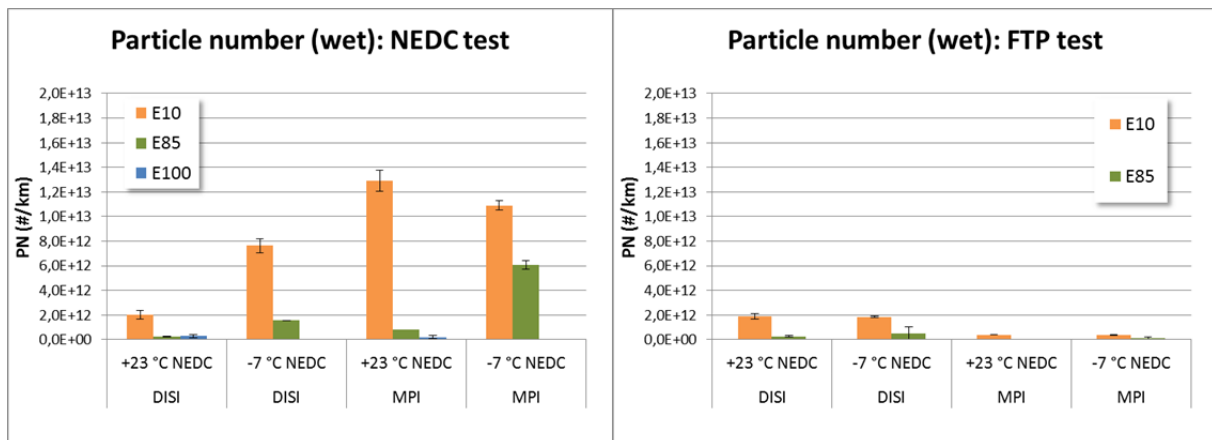


Figure 15. “Wet” particle number results.

Nucleation tendency was observed for the MPI car, which was seen also in high total wet PN results (Figure 16). Nucleation tendency was particularly strong when using E10 fuel. Accumulation mode particles dominated for the DISI car.

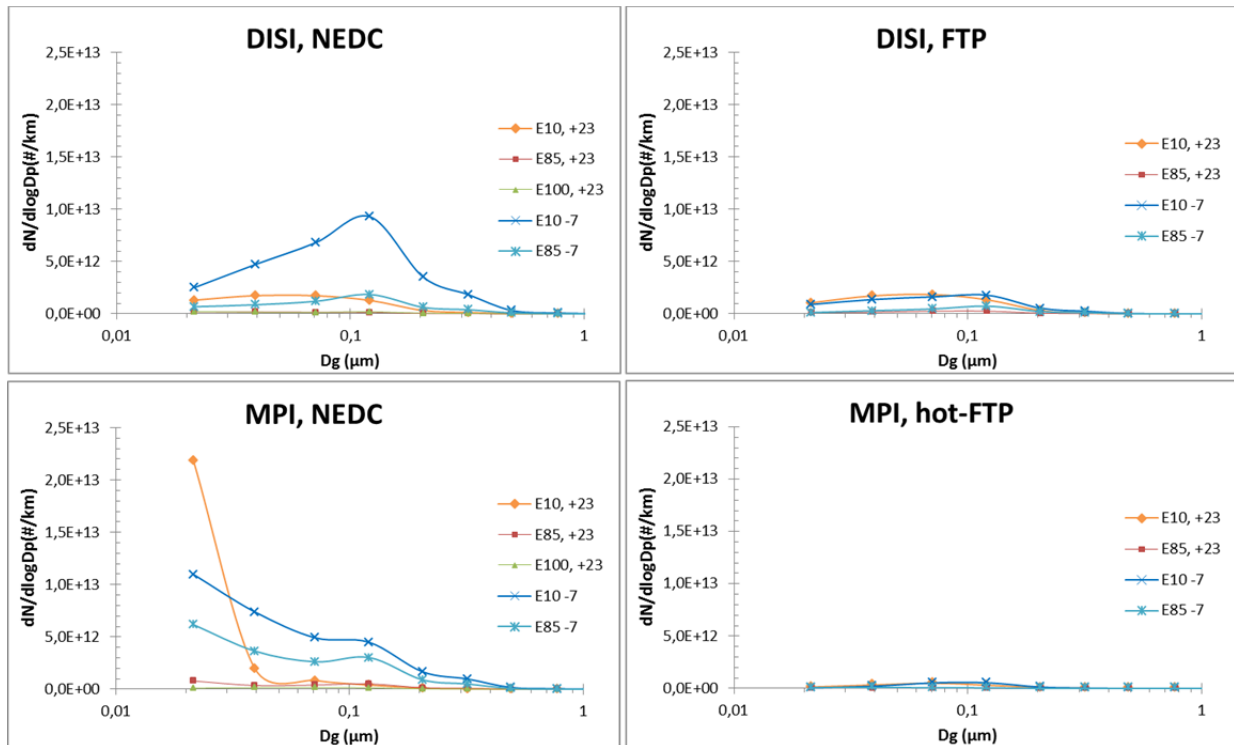


Figure 16. "Wet" particle number size distribution results.

Figure 17 shows driving cycle dependence of particles of two particle size classes, D_a 21.5 nm and D_a 71.3 nm. For the MPI car, particles in these size classes were formed in the accelerations and in the high-speed part of the NEDC test, whereas for the DISI car particles were concentrated in the accelerations.

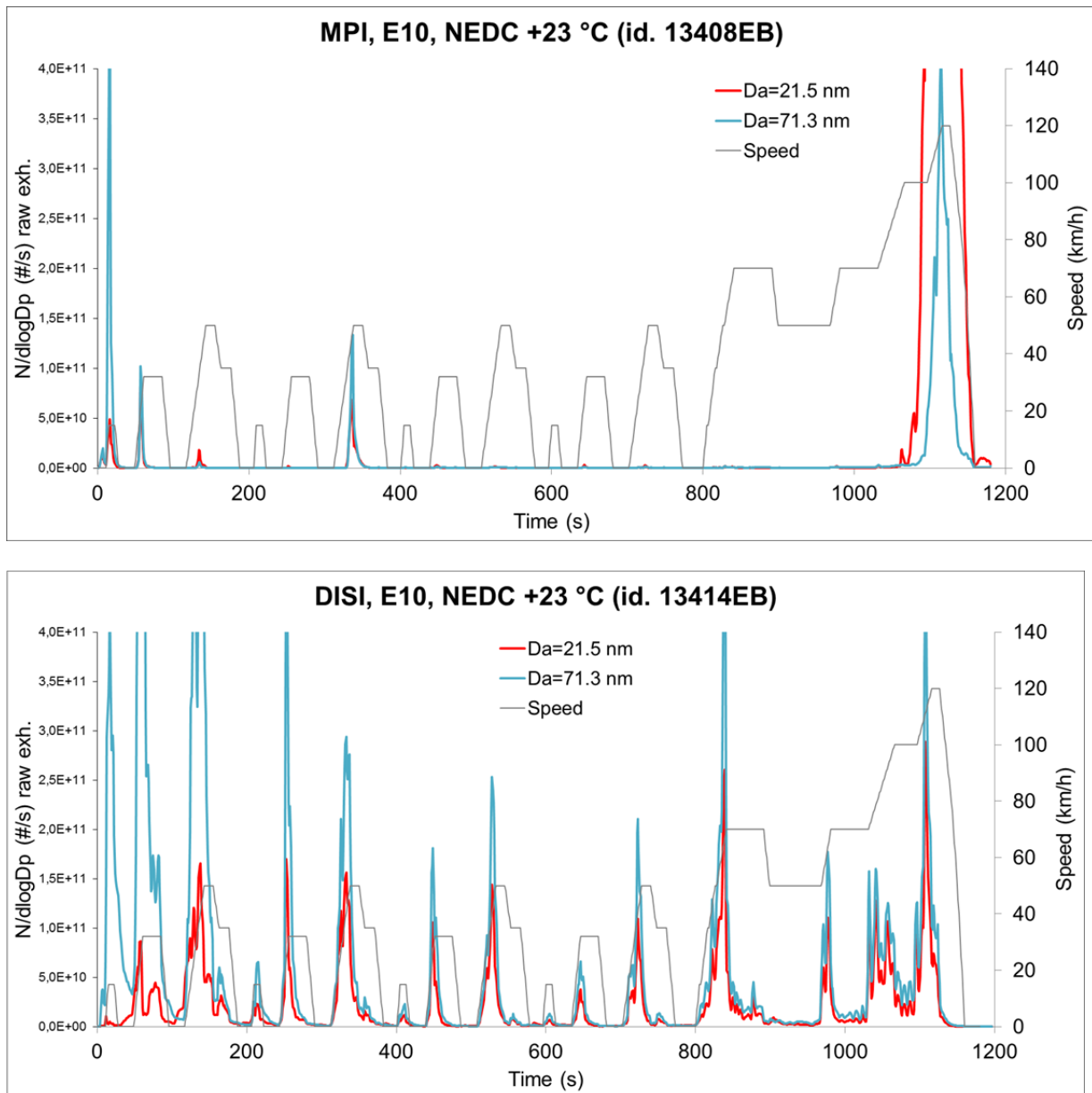


Figure 17. “Wet” particle number emissions at size classes of D_a 21.5 nm and 71.3 nm for MPI and DISI cars over the cold-start NEDC test.

3.5 E100 experiences

E100 was tested only at normal temperature, because cars would not start with E100 at temperatures lower than approximately 12 °C. Both cars experienced starting problems even at +23 °C when using the E100 fuel. These included long and difficult starting, stalling and hesitation. Serious starting and driveability problems were observed with E100 only in the beginning of test, whereas no problems occurred with warmed-up engine.

4. Discussion and summary

FFV cars are designed to be compatible with gasoline containing up to 85% ethanol (E85). This technology was studied within the Project “Research on Unregulated Pollutants Emissions of Vehicles Fuelled with Alcohol Alternative Fuels”, IEA AMF Annex 44. Operating Agent of project is China Automotive Technology and Research Center (CATARC). Several countries contributed with work to the project: China, Canada, Finland, Sweden, Israel and Switzerland. The final report of project will be prepared by CATARC. This report at hand describes Finnish contribution in Annex 44, which covered

- Two FFV cars: MPI and DISI
- Two temperatures: +23 °C and -7 °C
- Two cycles: cold-start NEDC and hot-start FTP75
- Three fuels: E10, E85 and E100 (E100 only at +23°C)
- Two tests per each car/fuel/cycle/temperature combination
- Various emissions studied: CO, HC, NO_x, PM, PN, speciated hydrocarbons, aldehydes, ammonia, N₂O etc.
- In-depth characterization of particles by the Finnish Meteorological Institute and Tampere University of Technology (to be published in scientific articles)

Summary of the selected results is shown in Figure 18. The effect of test temperature was evident for the most emissions. CO and HC emissions were higher at -7 °C than at +23 °C in the cold start NEDC test, particularly with the MPI car. E85 reduced the CO emission, but increased HC emissions when compared with E10. The dominating hydrocarbons present were methane, ethene, xylenes and acetylene for E85, whereas aromatics, methane and ethene dominated for E10. Ethanol emission was huge for the E85 fuel at -7 °C. Formaldehyde and acetaldehyde emissions were higher for the E85 fuel than for the E10 fuel in the cold-start NEDC test. Acetaldehyde was formed in substantial concentrations in 3 minutes after the cold-start of car, whereas emission level was low with warmed-up engine.

The NO_x emissions were relatively low over the NEDC test and only small differences between fuels were detected. Surprisingly high NO_x emissions were observed over the hot start FTP75 test, particularly after a 10 minutes pause. This indicates that cars may be optimised towards low CO and HC emissions at a cost of increased NO_x emissions. Nitrogen dioxide and nitrous oxide emissions were mostly below the detection limit of measurement equipment. In the opposite, ammonia emissions were substantial. Ammonia concentrations continuously exceeded 10 ppm, which is a limit value for SCR equipped heavy-duty engines, and even as high as 300-500 ppm concentrations were observed.

PM emissions were low: below 7 mg/km in the NEDC test and below 1 mg/km in the hot-start FTP75 test. However, a slight decrease in PM emission was observed with increasing ethanol content of fuel. “Wet” particle number emissions (PN) were higher at -7 °C than at +23 °C in the NEDC test, and higher for E10 than for E85. Nucleation tendency was seen for the MPI car, whereas accumulation mode particles dominated for the DISI car.

E100 was tested only at +23 °C temperature, because the startability limit of neat ethanol is only around +12 °C. Both cars experienced serious starting and driveability problems in the beginning of test with E100, whereas no problems occurred with warmed-up engine. The overall emissions were higher for E100 than for E85, though particle mass and number emissions were low.

E85 fuel typically reduces CO, HC, and NO_x emissions compared with gasoline at normal temperature, but not necessarily at low temperatures. Excess fuel is injected in cold starts due to the poor ignition of ethanol, which tend to increase for example acetaldehyde

emission before the engine is warmed-up at cold temperatures. Engine and emissions control technology of FFV cars are developing to overcome elevated cold-start emissions when using the E85 fuel, but the FFV cars in this study still showed a strong temperature-dependence. High emissions occurred only for the first kilometres after a cold-start, however, driving distances for gasoline cars are generally short in real-life. In sub-zero temperatures, block heaters could efficiently reduce cold-start emissions.

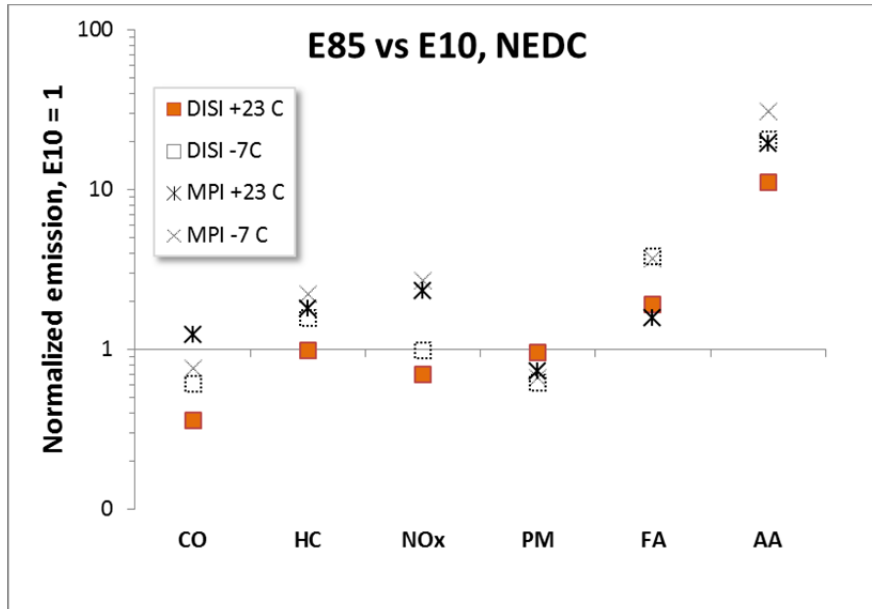


Figure 18. Summary of selected emission results over the NEDC test.⁴

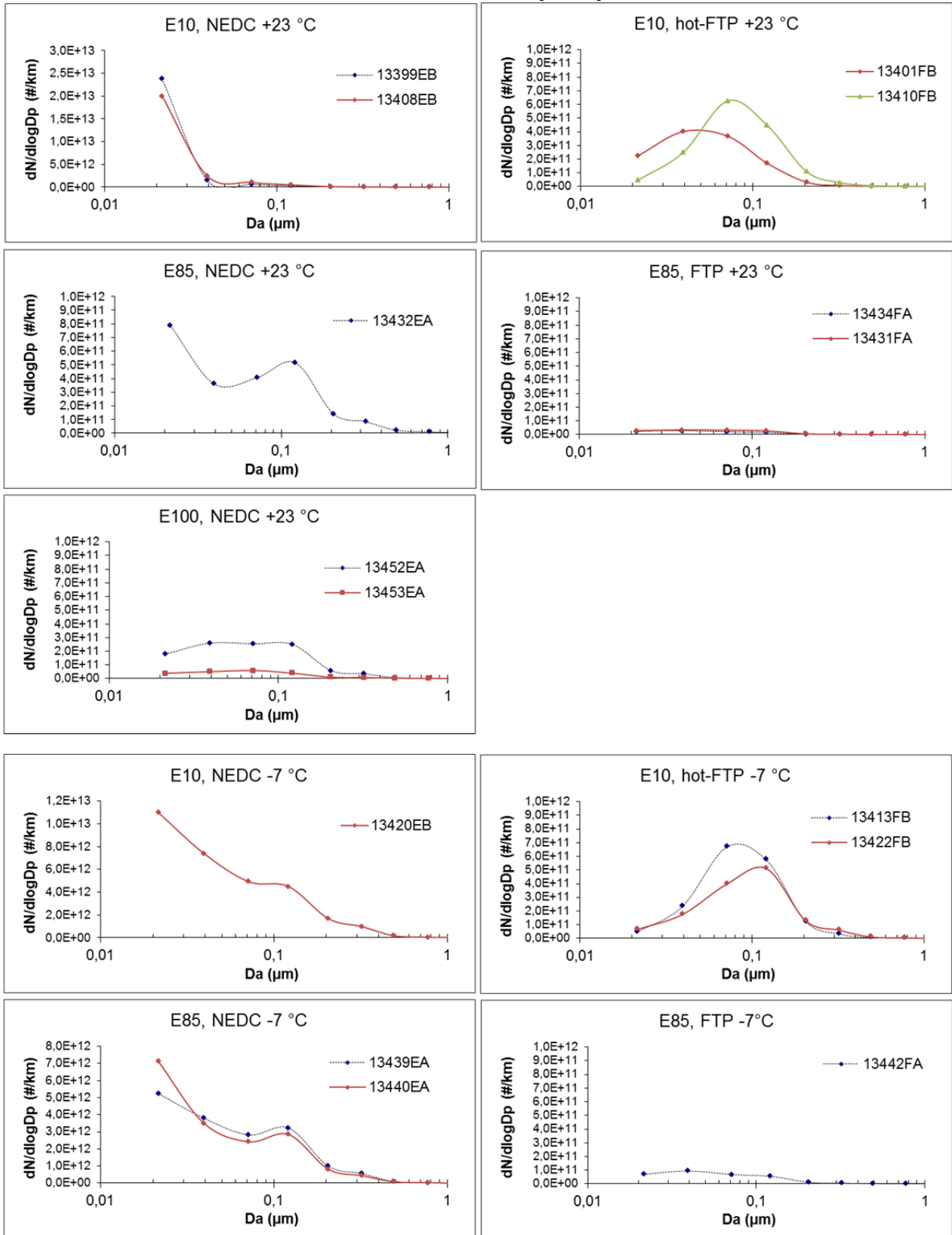
⁴ FA = Formaldehyde, AA = Acetaldehyde

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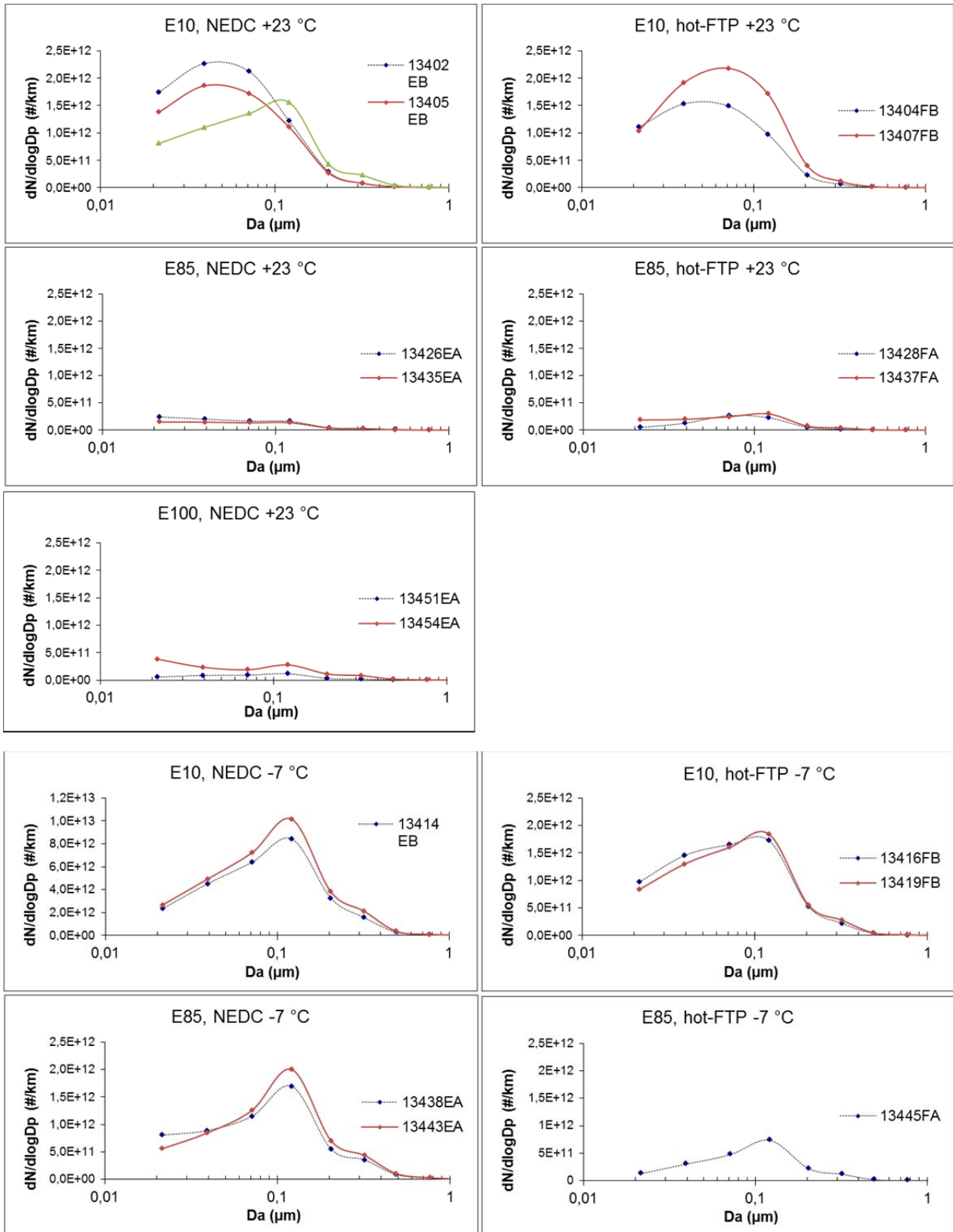
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APPENDIX 2. Particle size distributions (MPI).


Particle size distributions (DISI).



APPENDIX 3. Results in different test phases.

