**RESEARCH REPORT**

VTT-R-04308-14


# Unregulated emissions from Euro 5 emission level cars

Authors: Piritta Roslund, Päivi Aakko-Saksa, Päivi Koponen, and Jukka Nuottimäki

Confidentiality: Public

| Report's title | |
|---|---|
| Unregulated emissions from Euro 5 emission level cars | |
| **Customer, contact person, address**<br>TransEco research program | **Order reference** |
| **Project name**<br>EFFICARUSE | **Project number/Short name** |
| **Author(s)**<br>Piritta Roslund, Päivi Aakko-Saksa, Päivi Koponen, and Jukka Nuottimäki | **Pages**<br>25 |
| **Keywords**<br>Unregulated emissions, cars, Euro 5, E10, E85, diesel | **Report identification code**<br>VTT-R-04308-14 |

**Summary**

Unregulated emissions from nine Euro 5 emission level cars were studied over the European exhaust emissions driving cycle at +23 °C and -7 °C. The cars studied included two MPFI and two DISI gasoline cars using E10 fuel, two FFV cars using E10 and E85 fuels and three diesel cars equipped with diesel particulate filter (DPF).

Emissions typically increased when moving from +23 °C to -7 °C. The CO and HC emissions were mostly higher for spark-ignition cars than for diesel cars at both test temperatures. $NO_x$ emissions were higher for diesel cars than for spark-ignition cars. Methane and ethene were dominating C1–C8 hydrocarbons for E85 and diesel, whereas benzene, toluene, and xylenes were dominating for E10 fuelled cars. Particularly high aromatic emissions were seen for E10 fuelled FFV car at -7 °C. Aldehyde emissions were generally low for cars using E10. High acetaldehyde and ethanol emissions were observed for E85. Formaldehyde emissions were higher for cars using diesel or E85 than for cars using E10. Substantial catalyst chemistry dependent ammonia emissions were observed for spark-ignition cars, but not for diesel cars. The highest emissions of PM and priority PAHs were observed for E10 fuelled FFV cars, the second highest for the other E10 and E85 fuelled cars, and the lowest emissions for the DPF equipped diesel cars. Ames tests showed similar trend between the fuels. Similar trend between cars was seen for the Ames mutagenicity.

For many emission species, emissions were lower for newer cars (2013) than for older cars (2011). Gasoline hybrid emitted in many cases less than other spark-ignition cars. Some noticeable observations on unregulated emissions were gained, for example, unexpectedly high aldehyde emissions for some diesel cars.

| Confidentiality | Public |
|---|---|

23.9.2014

| Written by | Reviewed by | Accepted by |
|---|---|---|
| Roslund and Aakko-Saksa<br>Research Scientist | Juhani Laurikko<br>Principal Scientist | Nils-Olof Nylund<br>Research Professor |

**VTT's contact address**

P.O.Box 1000 (Biologinkuja 3-5), 02044 VTT

**Distribution (customer and VTT)**

TransEco research program

# Preface

A project, "Improving the energy efficiency of passenger car traffic through user-driven measures, EFFICARUSE" was carried out within the TransEco research program on energy efficiency and renewable energy in transportation. EFFICARUSE project focused on the research of energy efficiency aspects of cars by using an extensive set of cars, and those results are reported in the main report of the project. In the report at hand, focus is given on the unregulated emissions, which were measured for the selected cars of the EFFICARUSE test matrix. In addition to energy efficiency, exhaust emissions are an important factor affecting human health and environment in local and global scale.

TransEco research program is acknowledged for the possibility to conduct this interesting work. The Finnish Funding Agency for Innovations (Tekes) and the Ministry of Transport and Communications is acknowledged for granting the majority of the funding. The car importing agencies and companies are acknowledged for lending cars for testing. Personnel at VTT is acknowledged for their efforts in this work, particularly Reijo Mikkola, Tommi Hangasmaa, Erkki Virtanen, Pekka Piimäkorpi and Eija Skyttä.

Espoo, 23.9.2014

Authors

# 1. Introduction

In addition to energy efficiency, exhaust emissions are an important factor affecting human health and environment in local and global scale. Today, carbon monoxide (CO), total hydrocarbons (HC), nitrogen oxides ($NO_x$) and particulate matter (PM) and particle number (PN) emissions are regulated. Unregulated emissions from cars have traditionally been emphasised in relation to local pollution and health-effect issues. In this respect, species such as benzene, aldehydes, 1,3-butadiene and polyaromatic hydrocarbons (PAHs) are discussed. However, unregulated emissions have substantial impact also in global scale. Nitrous oxide ($N_2O$) and methane ($CH_4$) are well-known greenhouse gases. In addition, a number of emission species are acting as precursors in ozone forming process. Today, the Short-Lived Climate Pollutants (SLCP), namely black carbon, methane, tropospheric ozone, and hydrofluorocarbons, are discussed vividly as means to slow the rate of global warming over the near term. As a result, solid and extensive knowledge on unregulated emissions is needed to evaluate impact of transport sector in local perspective regarding human health and environment, as well as in global perspective regarding greenhouse gases, amongst others.

A project, “Improving the energy efficiency of passenger car traffic through user-driven measures, EFFICARUSE” was carried out within the TransEco research program on energy efficiency and renewable energy in transportation. In the EFFICARUSE project, the energy efficiency of an extensive set of cars was studied, and those results are reported in the main report. Unregulated emissions were studied with a part of the cars of the EFFICARUSE project. In this work, unregulated emissions at low temperature of -7 °C were studied in addition to the emissions at normal temperature of the type approval tests. Cars covered several types of spark-ignition cars: gasoline, gasoline hybrid and E85 fuelled cars. In addition, three diesel cars were tested. The more extensive introduction is presented in the main report of the EFFICARUSE project.

# 2. Description and methods

Test fuels matrix comprised of the following fuels:

- Commercial E10 gasoline: max. 10% ethanol containing gasoline
- RE85 containing 85% ethanol and 15% gasoline
- Commercial diesel fuel

**Cars**

In total 21 cars were tested in the main project. Unregulated emissions were measured for nine cars, which were of model year 2011 and 2013, representing Euro 5 emission level cars. More detailed description of cars is given in the main report. Abbreviations used for the cars in this report are given in Table 1. Three measurement campaigns were carried out in 2011 and 2013, as described in the main report.

*Table 1. Test cars, fuels and measurements conducted in the project for unregulated emissions.*

| Car | Year, type | Abbreviation | Fuels | Emissions at +23 and -7 °C |
|---|---|---|---|---|
| Toyota Auris 1.6 Valvematic | 2011, MPFI | MPFI TA | E10 | CO, HC, $NO_x$ |
| Toyota Auris HSD | 2011, hybrid | MPFI hybrid TA | E10 | Speciated hydrocarbons (C1-C8) |
| Volkswagen Golf 1.2 TSI | 2011, DISI | DISI VW | E10 | |
| Alfa Romeo Giulietta | 2011, DISI | DISI AR | E10 | |
| Volkswagen Passat MultiFuel | 2011, FFV | FFV VW | E10, E85 | Aldehydes (11) |
| Volvo V70 T4F | 2013, FFV | FFV V | E10, * | |
| Volkswagen Golf BlueMotion 1.6 TDI | 2011, diesel | Diesel VW | Diesel | FTIR analysis** |
| Volvo V70 D2 | 2013, diesel | Diesel V | Diesel | PAHs and Ames tests *** |
| Mercedes Benz B200 CDI | 2013, diesel | Diesel MB | Diesel | |

*E85 tested only at +23 °C, **) Part of FTIR results rejected due to leak in the system
***) Samples obtained at +23 and -7 °C combined for diesel cars due to low PM mass.

**Test procedure**

Cars were tested on a chassis dynamometer in a climatic test cell at +23 °C and at -7 °C according to the European exhaust emissions driving cycle (UN ECE R83). Driving cycle, which totals 11.0 km, was divided into three test phases to study emissions behavior at cold start and with warmed-up engines. The first and second test phases each consisted of 2.026 km driving (ECE15), and the third test phase, the extra-urban driving cycle (EUDC), was 6.955 km. 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.

**Gaseous emissions**

Equipment used in the measurement of the CO, HC, and $NO_x$ emissions conforms to the specifications of the UN ECE R83. 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. This matter is discussed by Sandström-Dahl et al. 2010 and Aakko-Saksa et al. 2011a. The calculation method chosen here uses the density of 0.619 $g/dm^3$, and therefore results in lower HC emissions for the E85 fuel than does the EC regulation 692/2008 method.

Aldehydes were collected from the CVS diluted exhaust gas using 2,4-dinitrophenylhydrazine (DNPH) cartridges. The DNPH derivatives were extracted with an acetonitrile/water mixture and analyzed using HPLC technology (Agilent 1260, UV detector, Nova-Pak C18 column). Aldehydes reported are formaldehyde, acetaldehyde, acrolein, propionaldehyde, crotonaldehyde, methacrolein, butyraldehyde, benzaldehyde, valeraldehyde, *m*-tolualdehyde, and hexanal.

The diluted exhaust gas for analysis of C1 to C8 hydrocarbons was collected from the same Tedlar bags that were 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 analyzed are methane, ethane, ethene, propane, propene, acetylene, isobutene, 1,3-butadiene, benzene, toluene, ethyl benzene and *m*-, *p*-, and *o*-xylenes.

A number of compounds, amongst others ethanol ($CH_3CH_2OH$), ammonia ($NH_3$) and nitrous oxide ($N_2O$), were measured on-line at one-second intervals using Fourier Transformation Infra-Red (FTIR) equipment (Gasmet Cr-2000) in 2011.

**Particulate matter**

Particles were collected with a high-capacity sampler, which was developed in 1990s for measurements of gasoline cars (Kokko et al. 2000). The high-capacity collection system 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 masses of particles. The filter type was Fluoropore 3.0 µm FSLW. A Sartorius SE2-F microbalance was used for weighing. In these measurements, the flow was 850–1000 liters/minute and two Ø142 mm filters were used in parallel. Particulate filters from different measurement campaigns were stored in freezer, and sent for further analysis (PAH, Ames) at the same time. Due to very low amounts of PM in diesel emissions, the samples of +23 °C and -7 °C for the Ames assay were combined.

**Soxhlet extraction**

Soxhlet extraction with dichloromethane was conducted for the particle filter samples before PAH analyses and the Ames test. Several filters were combined for each extraction batch. An equivalent number of filters were extracted for the blank control sample. Filters were protected from light during and after the Soxhlet treatment to avoid unwanted changes in the samples. The Soxhlet apparatus was cleaned by solvent extraction (6 hours). An internal standard was added, and samples were Soxhlet extracted for 16 hours. The volume of extract was reduced by evaporating the solvent, and the concentrates were divided for the PAH analyses and Ames tests. For the Ames test, the dichloromethane solvent was replaced by dimethyl sulphoxide (DMSO), which is better tolerated by the test organisms used in the Ames assay.

**Polyaromatic hydrocarbons (PAHs)**

A total of 31 individual PAH compounds were analyzed from the Soxhlet extracted particle samples using GC/SIM-MS following purification of the extract by liquid chromatography. EPA 610 PAH mixture from Supelco and PAH-MIX 63 from Ehrensdorf were used to check the calibration standard, which was made from pure solid substances of each PAH compound determined. Detection limits were 0.1 µg component/sample, which represents approximately 0.05 µg/km for the DISI cars, 0.09 µg/km for the MPFI car, 0.05 µg/km for the MPFI hybrid car, 0.07 µg/km for the FFV cars with E10 and with RE85, and 0.03 µg/km for the diesel cars. In our work, from 31 PAHs analyzed seven PAHs defined in a list of mobile-source air toxics by US EPA (2007) are reported:[1] benzo[*a*]anthracene (BaA, Group 2B), chrysene (Chr, Group 2B), benzo[*b*]fluoranthene (BbF, Group 2B), benzo[*k*]fluoranthene (BbF, Group 2B), benzo[*a*]pyrene (BaP, Group 1), 7,12-dimethylbenz[*a*]anthracene and indeno[1,2,3-*cd*]pyrene (IP, group 2B). Sum of 14 priority PAHs (PAH14) also included fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[*e*]pyrene, dibenzo[*a,h*]anthracene, and benzo[*g,h,i*]perylene, whereas 7,12-dimethylbenz[*a*]anthracene was excluded.

[1] There are several lists of "Priority PAHs" to describe the cancer-related risks of substances, for example a list of mobile-source air toxics by US EPA (2007) and European directive 2004/107/EC for monitoring ambient air. IARC has classified PAHs as carcinogenic (group 1), probably carcinogenic (group 2A) or possibly carcinogenic (group 2B) (IARC 2008, 2011).

**Ames test**

The test was performed using the method VTT-4352-91 which is based on the methods of Maron, D.M. and Ames, B.N. (1983) Mutat. Res., 113, 173–215 and recommendations of OECD (OECD Guidelines for Testing of Chemicals, Paris, Test Number 471, adopted 1983, updated 1997). The tester strains used in the assessment was *Salmonella typhimurium* strain TA98 and TA98NR. The tester strain TA98 used in the assessment is sensitive to frameshift-type mutagens. To enable indirect mutagens, which are mutagenic in mammals only after metabolic activation, also to be detected, a metabolic activation system was incorporated in the test procedure by using TA98 strain with metabolic activation (+S9). Samples from two FFV cars and a DISI car were tested also for direct mutagenicity with TA98 strain without metabolic activation (-S9).The contribution of nitro-PAH-type compounds to mutagenicity can be studied using the tester strains TA98 and the nitroreductase-deficient TA98NR in parallel. Provided the sample exhibits direct mutagenicity against TA98 but not against TA98NR, the presence of nitro-PAHs is likely. For example, polycyclic aromatic hydrocarbons, PAHs, show indirect mutagenicity, whereas nitro-PAHs are direct-acting mutagens.

In this study, the samples were tested both for direct (-S9mix) and indirect (+S9mix) mutagenicity at five or six dose levels corresponding to particle masses ranging from 0.1 to 1.0 mg/plate. Depending on the amount of PM mass available, the tests were carried out using replicate plates (1 – 3) for each dose level. For metabolic activation a S9 homogenate prepared from rat livers induced with phenobarbital and β-naphtoflavone was used. The volume of liver homogenate was 20 µL per plate. 4-Nitroquinoline (0.5 µg/plate) and 2-aminoanthracene (0.5 µg/plate) were used as the positive control samples for direct and indirect mutagenicity, respectively. DMSO (100, 200 and 300 µl per plate) was used as the solvent control. The mutagenic dose response of each sample was calculated by linear regression analysis. The slope (b) within the linear part of regression line ($y = bx + a$) describes the magnitude of mutagenic activity, and is expressed as revertants/mg of sample. Only the responses obtained at non-toxic concentration levels were included in the calculations. On the basis of the specific mutagenic response of each sample (rev/mg) and the amount of particulate matter (mg PM/km) generated by each vehicle/fuel type, theoretical estimates for the mutagenic emissions in distance-based unit (krev/km) were calculated.

# 3. Results

## 3.1 Gaseous Emissions and PM

Highest CO emissions were found for FFV VW with E10 at both +23 °C and -7 °C test temperatures. The highest HC emissions were found for FFV V at +23 °C and for FFV VW at -7 °C when using RE85 fuel (**Figures 1** and **2**). All tested cars had CO emissions below the new Euro 6 limits at +23 °C (1000 mg/km for gasoline and 500 mg/km for diesel cars). The lowest CO and HC emissions at -7 °C were detected for diesel cars at -7 °C. This was emphasized at -7 °C when emissions from spark-ignition cars increased substantially.

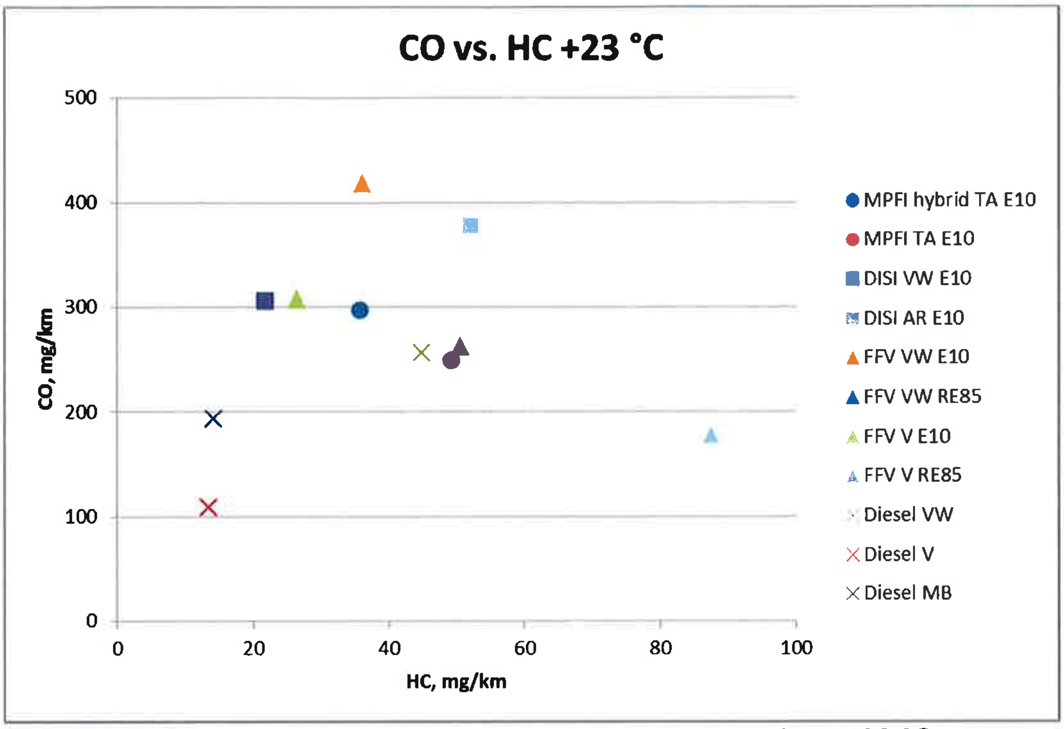



*Figure 1. CO and HC emissions over the European test cycle at +23 °C.*

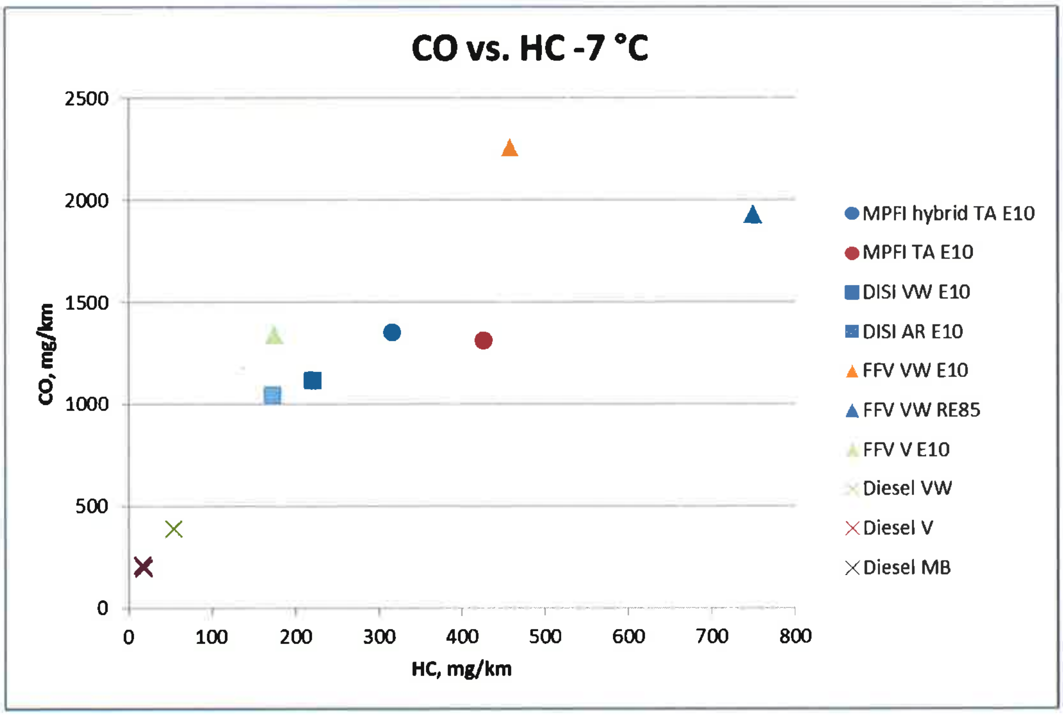



*Figure 2. CO and HC emissions over the European test cycle at -7 °C.*

$NO_X$ emissions detected for the diesel cars were higher than those for the spark-ignition cars at both temperatures (**Figure 3** and **4**). Diesel V had especially high $NO_x$ emissions. Two of the diesel cars (VW and MB) had their $NO_X$ emissions close to Euro 5b level (180 mg/km), whereas $NO_x$ emission from diesel V, 440 mg/km, clearly exceeded Euro 5b limit at +23 °C.

$NO_X$ emission levels at -7 °C were several times higher than at +23 °C for all the diesel cars. $NO_x$ emissions from the spark-ignition cars were low at both test temperatures.

The highest PM emissions were measured for the two FFV cars (V, VW) and DISI VW with E10 at +23 °C and at -7 °C (**Figures 3** and **4**). PM emissions were below the Euro 5 and 6 (5 mg/km) limits with all the cars at +23 °C. DISI VW had PM emission of 7.3 mg/km at -7 °C. PM emissions were 5 – 7 times higher at -7 °C than at +23 °C for the FFV V and FFV VW with E10 fuel (13.2 and 13.8 mg/km). Significantly lower PM emission level was observed for these cars when using RE85 fuel, i.e. 2.8 mg/km at -7 °C.

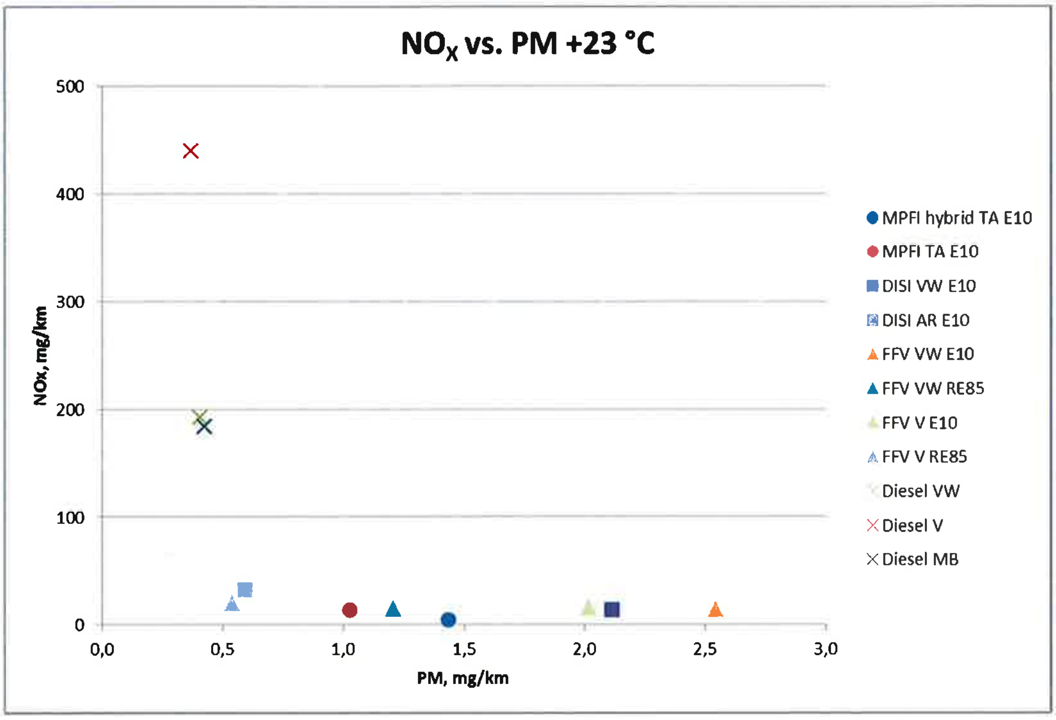



*Figure 3. $NO_x$ and PM emissions over the European test cycle at +23 °C.*

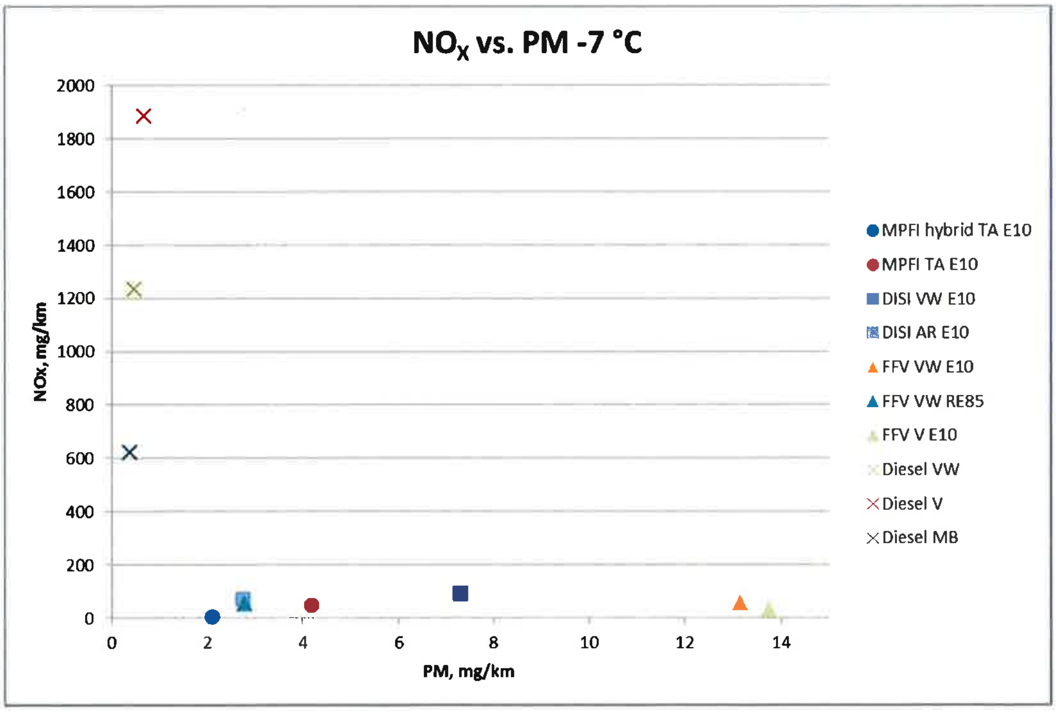



*Figure 4. $NO_x$ and PM emissions over the European test cycle at -7 °C.*

Methane, ethene, benzene, toluene, and xylenes were dominating C1–C8 hydrocarbons with E10 fuel for the spark-ignition cars at +23°C and at -7 °C (**Figures 5** and **6**). For the turbocharged DISI AR and DISI VW, toluene and xylenes emissions were notably lower than for MPFI TA at -7 °C with E10. In **Figure 7** BTEX-levels for all the cars are presented. The highest BTEX-level at +23 °C had DISI AR (17.8 mg/km) and the highest BTEX-levels at -7 °C had FFV V and MPFI TA with E10 fuel (141.0 mg/km and 132.7 mg/km).

With RE85 fuel methane and ethene emissions were the dominating C1–C8 hydrocarbons. Sum of the methane and ethene emissions was higher for the E85 fuelled FFV than for any other spark-ignition car at both test temperatures. With FFV VW C1–C8 emissions were clearly higher (almost double) than for the newer technique FFV V at -7 °C with E10.

Generally, C1–C8 hydrocarbon emissions from the diesel cars were low when compared with the spark-ignition cars at -7 °C, whereas at +23 °C differences between cars were rather small. For the diesel cars, methane and ethene were the main C1–C8 hydrocarbons at both temperatures. For the model 2013 diesel cars (V and MB) ethene emissions were clearly lower than those for the year 2011 diesel car (VW).

Emission level of 1,3-butadiene was very low with all the cars tested, in maximum 1.9 mg/km at -7 °C for FFV VW with E10 fuel (**Figures 5** and **6**).

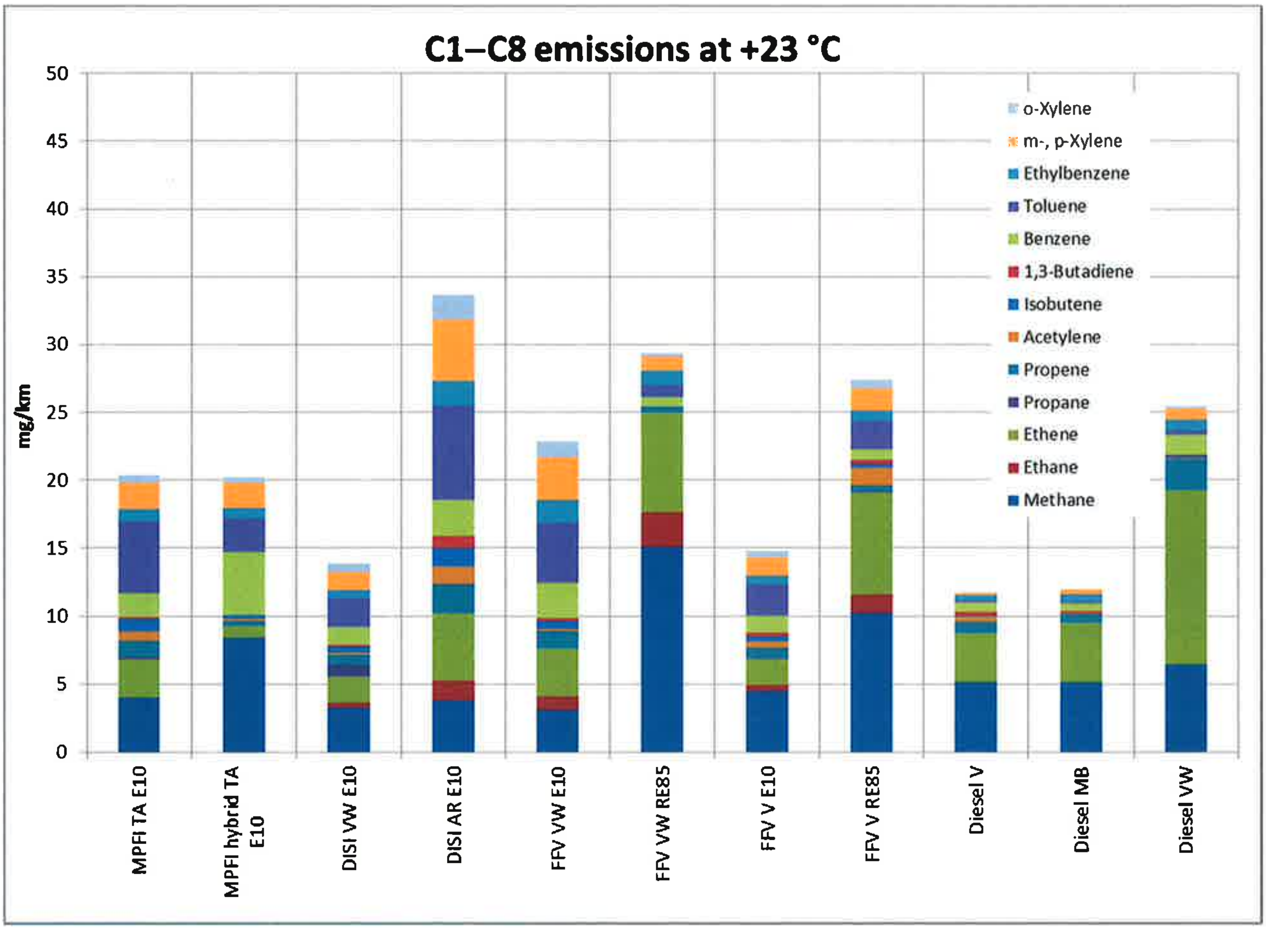



*Figure 5. C1–C8 hydrocarbon emissions over the European test cycle at +23 °C.*

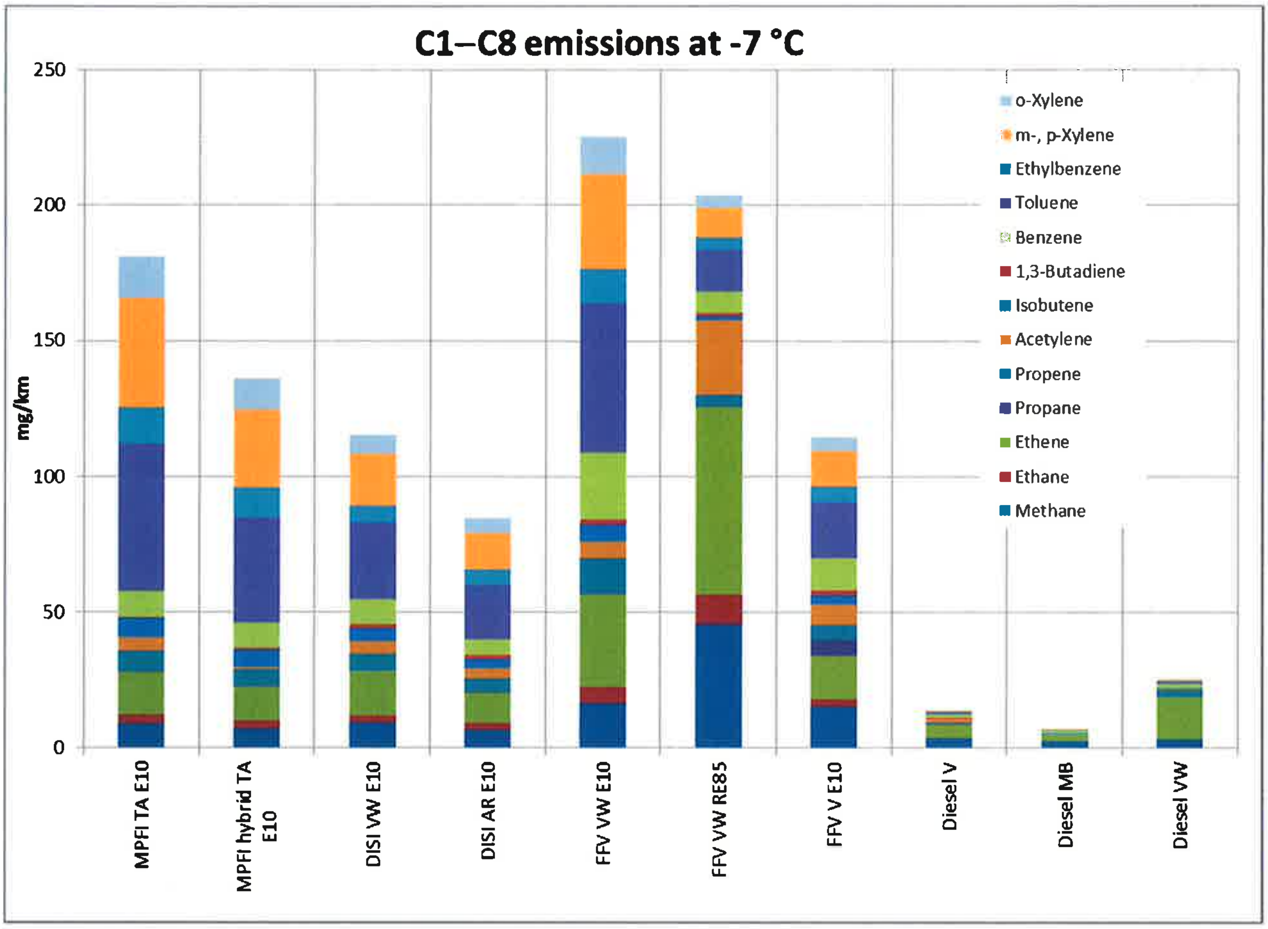



*Figure 6. C1–C8 hydrocarbon emissions over the European test cycle at -7 °C.*

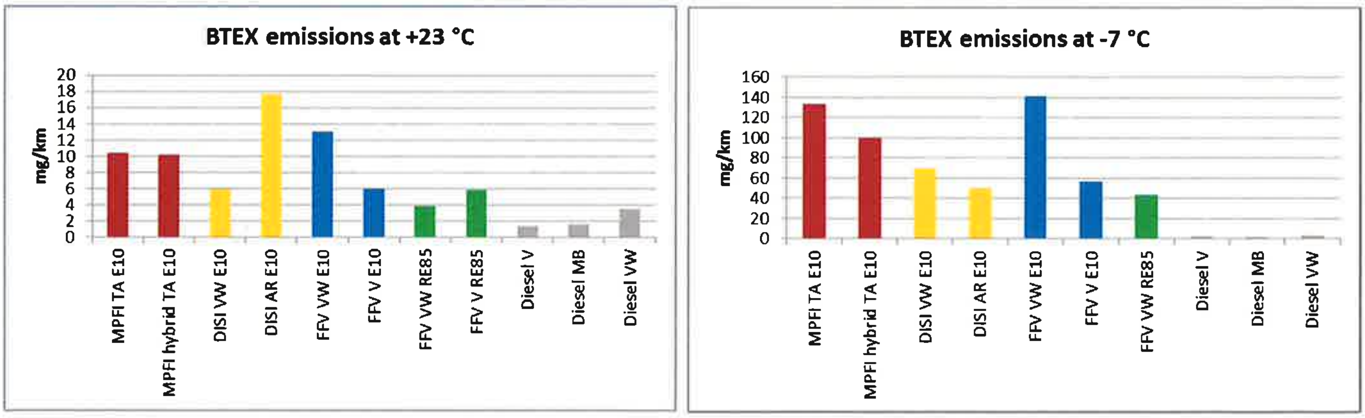



*Figure 7. BTEX emission levels over the European test cycle at +23 °C and -7 °C.*

Aldehyde emissions were low for the spark-ignition cars with E10, though acetaldehyde and formaldehyde emissions increased when moving from +23 to -7 °C for other E10 fuelled cars than MPFI hybrid TA whose formaldehyde emission stayed at the same very low level at both temperatures. When using the RE85 fuel, both formaldehyde and acetaldehyde emissions increased as the test temperature decreased from +23 to -7 °C; increase in acetaldehyde emission was especially significant for FFV VW (from 8.0 mg/km to 52.6 mg/km). With RE85 fuel for FFV VW, also benzaldehyde and crotonaldehyde emissions were notable at -7 °C (**Figures 8** and **9, Appendices**).

Formaldehyde emissions for the diesel cars were higher than for the most MPFI and DISI cars using E10. Though clear difference in aldehyde emissions for the newer technique 2013 car (V and MB) and older technique 2011 car (VW) can be detected. That is, aldehyde emissions in general were higher for older diesel car (VW 2011) than for newer diesel cars at both temperatures (overall, 3 – 10 times higher) (**Figure 8**). Altogether, older diesel car had higher aldehyde emissions at both temperatures than any other diesel car or E10 fuelled car; only RE85 resulted in higher aldehyde emissions than this diesel car.

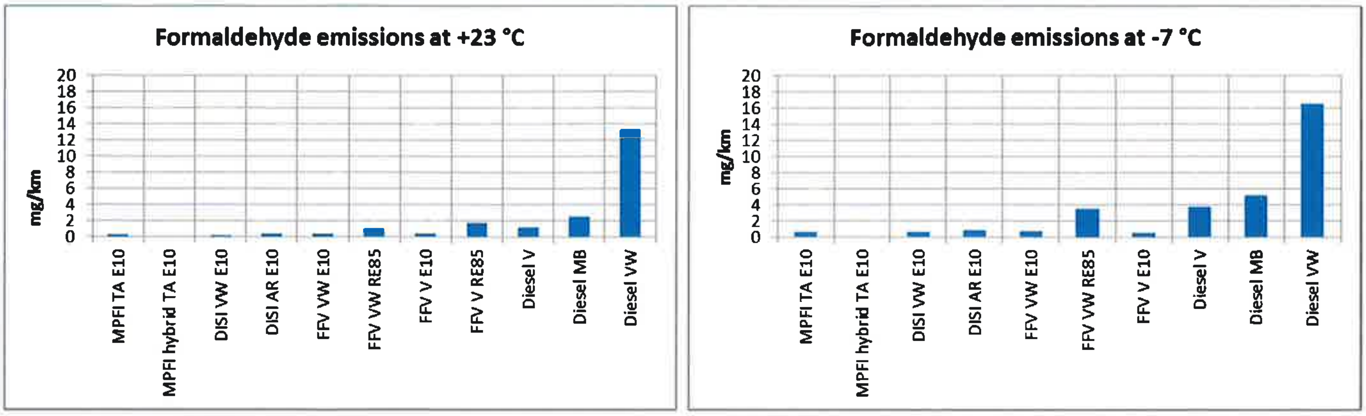



*Figure 8. Formaldehyde emissions over the European test cycle at +23 °C and -7 °C.*

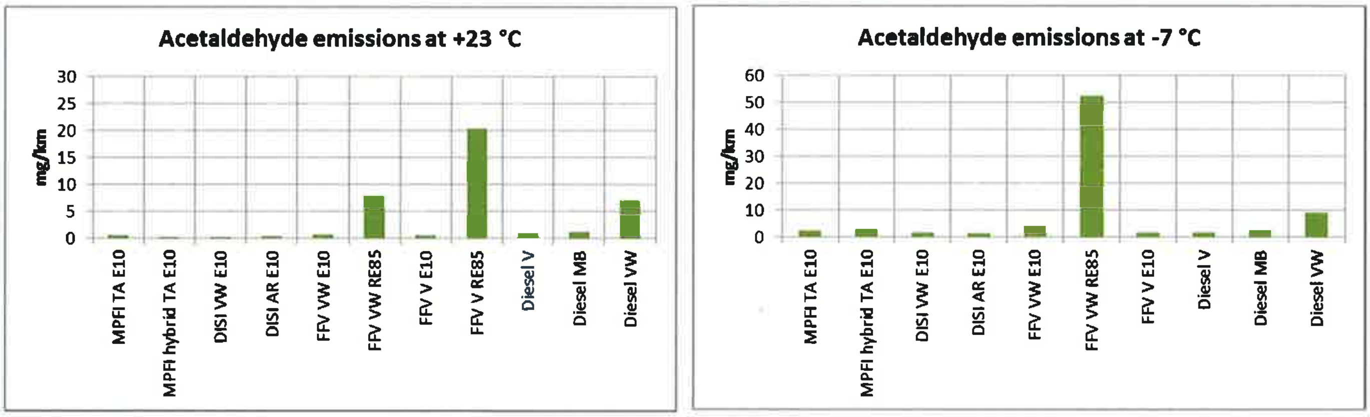



*Figure 9. Acetaldehyde emissions over the European test cycle at +23 °C and -7 °C.*

**FTIR results**

A number of compounds, amongst others ethanol ($CH_3CH_2OH$), ammonia ($NH_3$), and nitrous oxide ($N_2O$), were measured on-line at one-second intervals using Fourier Transformation Infra-Red (FTIR) equipment (Gasmet Cr-2000) in 2011. Some results for ethanol, ammonia, and nitrous oxide are presented in **Figure 10**.

The highest ethanol emission was detected for FFV VW especially at -7 °C with E85. Ethanol was not measured with FTIR for other cars.

The highest ammonia emission was detected also for FFV VW at -7 °C (46.8 mg/km) with E10.

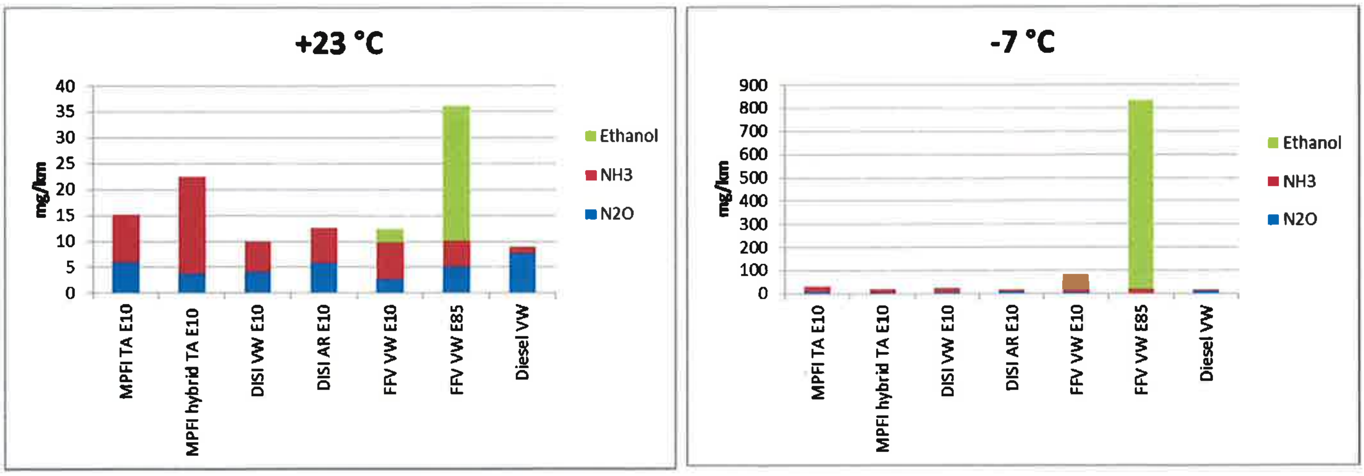



*Figure 10. FTIR results for the selected gaseous emissions over the European test cycle at +23 °C and at -7 °C*

## 3.2 PAH and mutagenicity

Particle-associated priority PAH emissions are shown as distance-based terms in **Figures 10–12**. For the spark-ignition cars particulate mass allowed detailed analysis at both test temperatures. PAH and Ames results for FFV V at -7 °C are an average from parallel analyses, all other results are from single samples. For the diesel cars particulate mass was so low that the samples from two temperatures (+23 and -7 °C) were combined for PAH analyses and Ames tests. PAH 7 emissions as average results from +23 and -7 °C are presented for all cars in **Figure 11** to achieve valid comparison with the diesel cars. In addition, PAH 7 emissions for spark-ignition cars are shown separately at both test temperatures in **Figures 12** and **13**.

When 7 priority PAHs are considered, the most dominant priority PAHs were benzo[*a*]pyrene, benz[*a*]anthracene, benzo[*b*]fluoranthene and indeno[1,2,3-*cd*]pyrene. PAH 7 emissions at +23 °C were considerably lower for all the cars tested than at -7 °C. When considering the 14 priority PAHs, the most dominant PAH was pyrene at both temperatures.

Priority PAH emissions were high for the FFV cars when using E10 as fuel, whereas significantly lower emission was observed for the RE85 fuel at both +23 °C and -7 °C temperatures (**Figures 12** and **13**). Priority PAH emissions were also notably low for MPFI hybrid TA both at +23 °C and -7 °C, the lowest for the spark-ignition cars with E10 fuel. The sum of 7 priority PAHs at +23 °C for spark-ignition cars were 0.1 – 1.3 µg/km, whereas 4.5 – 43 µg/km at -7 °C excluding MPFI hybrid TA with very low emissions: PAH 7 only 0.5 µg/km at -7 °C.

Priority PAH emissions for the diesel cars were low, below 0.10 µg/km for combined sample from the tests at +23 and -7 °C, whereas for the spark-ignition cars the lowest emissions were 0.14 µg/km for the MPFI hybrid TA with E10 and with RE85 the lowest emissions were 0.10 µg/km for FFV V at +23 °C.

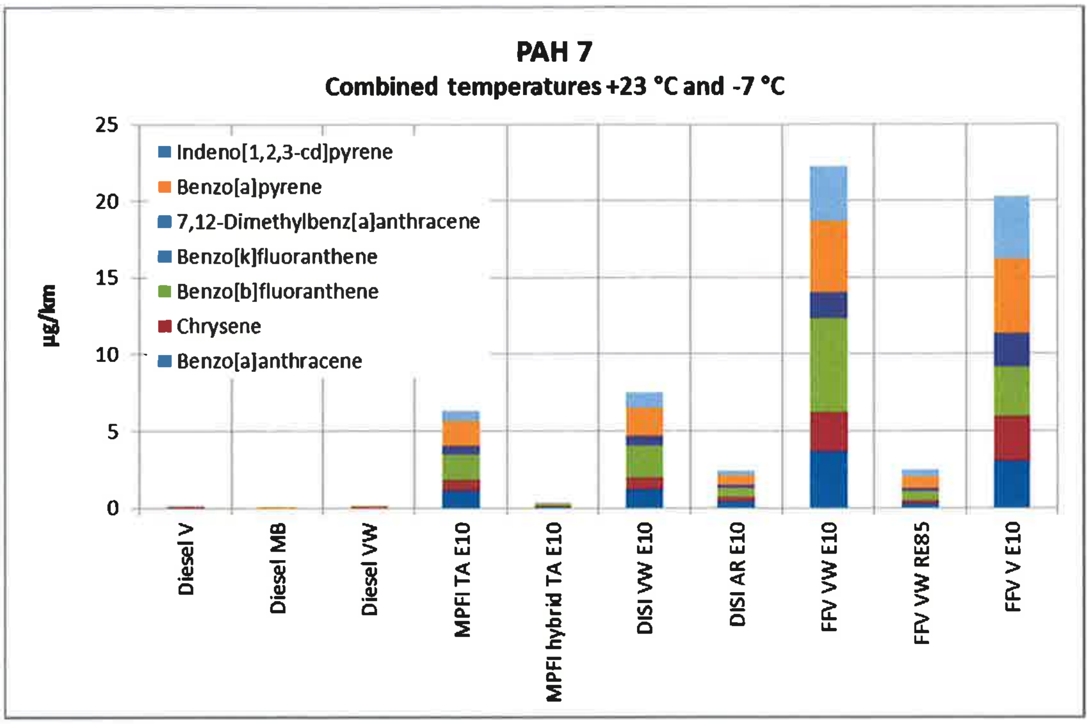



*Figure 11. Selected PAH emissions over the European test cycle as an average of tests at combined temperatures +23 °C and -7 °C.*

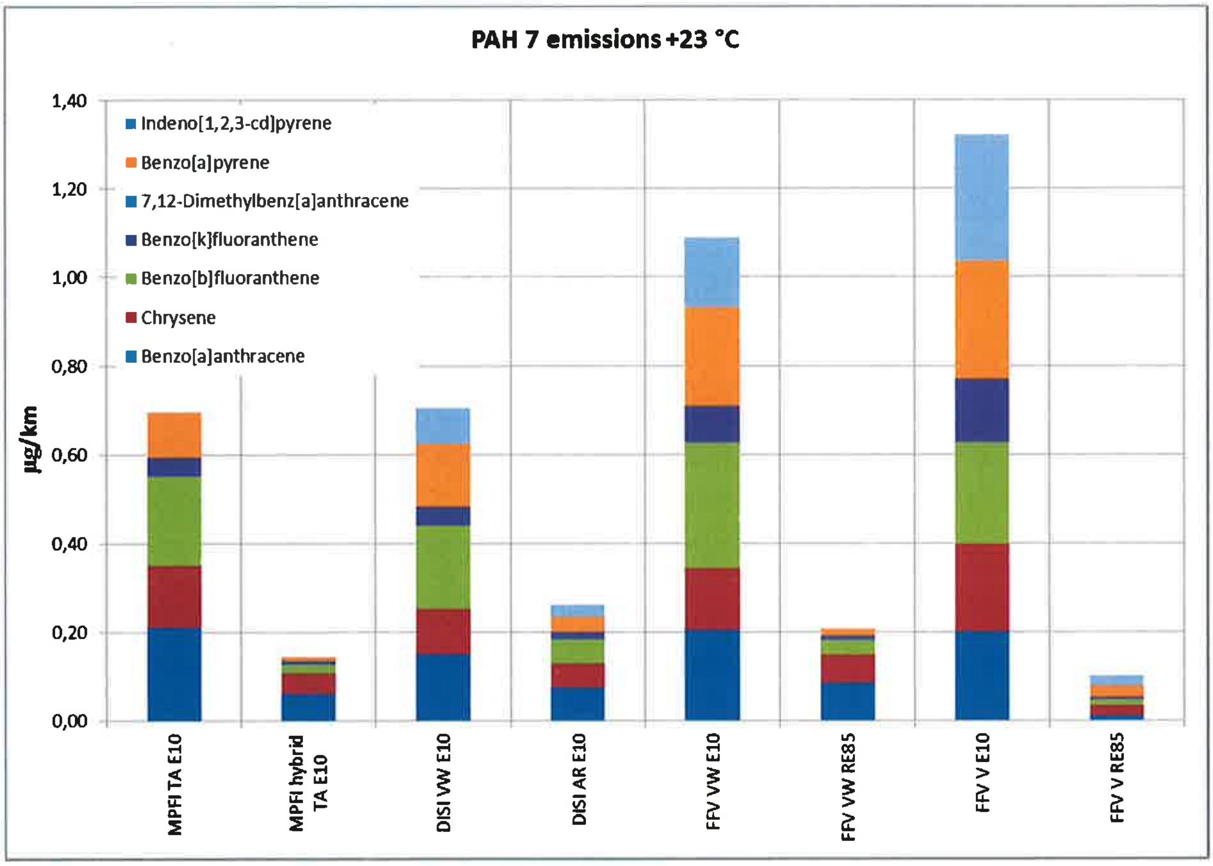



*Figure 12. Selected PAH emissions over the European test cycle at +23 °C.*

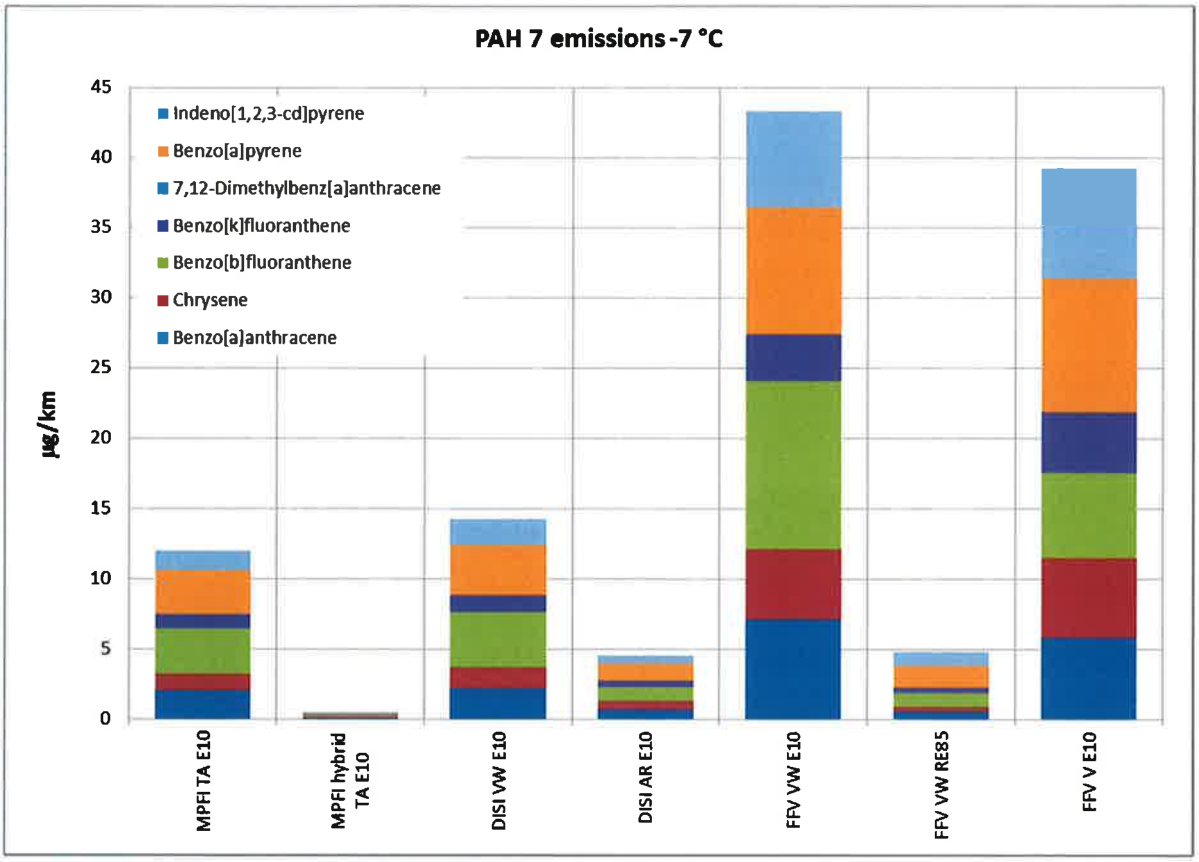



*Figure 13. Selected PAH emissions over the European test cycle at -7 °C.*

Although the specific indirect mutagenicity (TA98+S9; rev/mg) of the PM emissions from the diesel cars was extremely high (approximately up to 3500 rev/mg), due to low emission amounts per km (mg/km PM), indirect mutagenicity responses of diesel cars in terms of krev/km were negligible (**Figure 14**). At -7 °C, the highest PM associated indirect mutagenicity was exhibited by E10 fuelled the FFV cars and DISI VW. This is largely attributable to the higher PM emissions generated per km by these vehicles than by the diesel cars.

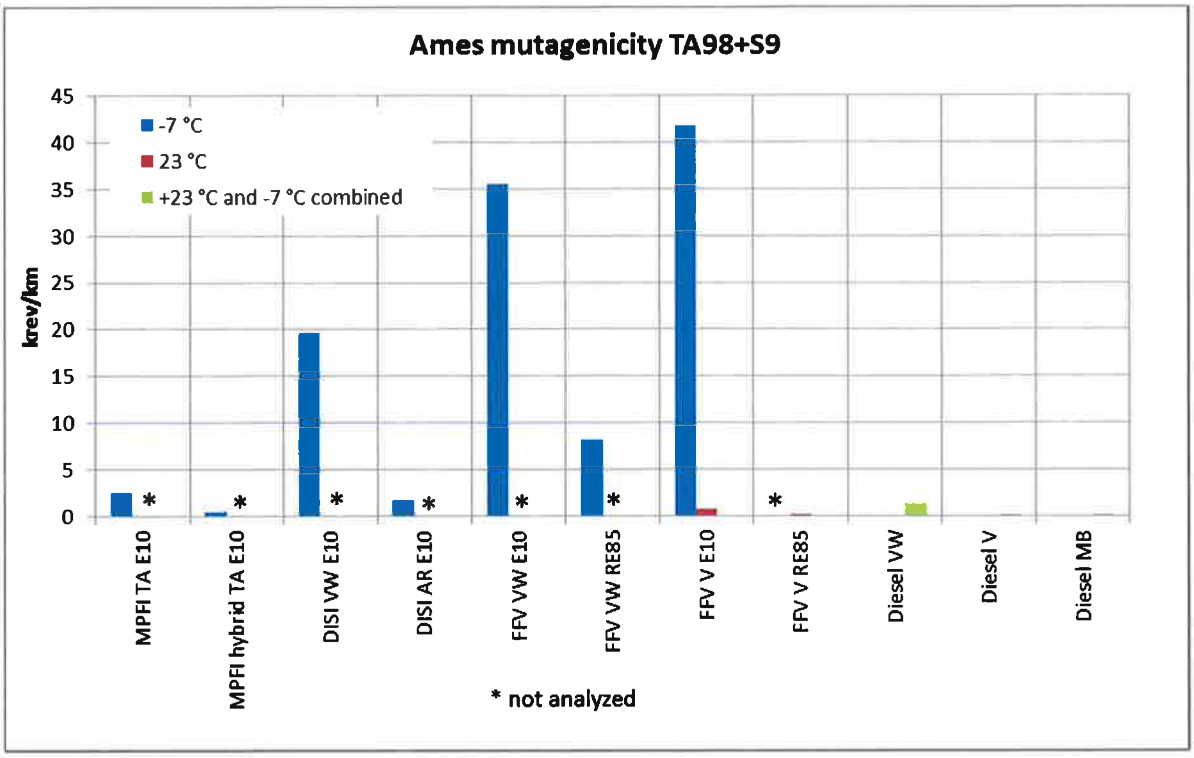



*Figure 14. Indirect mutagenicity (TA98+S9) of PM emissions generated by different vehicles and fuels. For the diesel cars the results are average at combined +23 °C and -7 °C.*

Polycyclic aromatic hydrocarbons (PAH) show indirect mutagenicity, i.e. only after metabolic activation (+S9 mix), whereas nitro-PAHs are direct-acting mutagens. The contribution of nitro-PAH-type compounds to mutagenicity can be studied using tester strains TA98 and the nitroreductase-deficient TA98NR in parallel. Provided the sample exhibits direct mutagenicity in TA98 but not in TA98NR, the presence of nitro-PAHs is likely.

In addition to tests with TA98 strain with metabolic activation (+S9), a few of the samples were similarly assessed for mutagenicity with TA98 strain without metabolic activation (-S9 mix), and tested also with the nitro-PAH-deficient strain TA98NR (-S9 mix), in parallel (**Figure 15**). The results obtained indicate that the role of indirect-acting mutagens is substantial when compared to direct-acting mutagens. The results also indicated that nitro-PAHs were not present in the DISI WV and FFV V particles. Some indication of potential presence nitro-PAHs could only be shown by the PM emissions of the FFV VW car (TA98: 1443 rev/mg vs. TA98NR: 360 rev/mg; 19 krev/km vs. 4.8 krev/km, respectively).

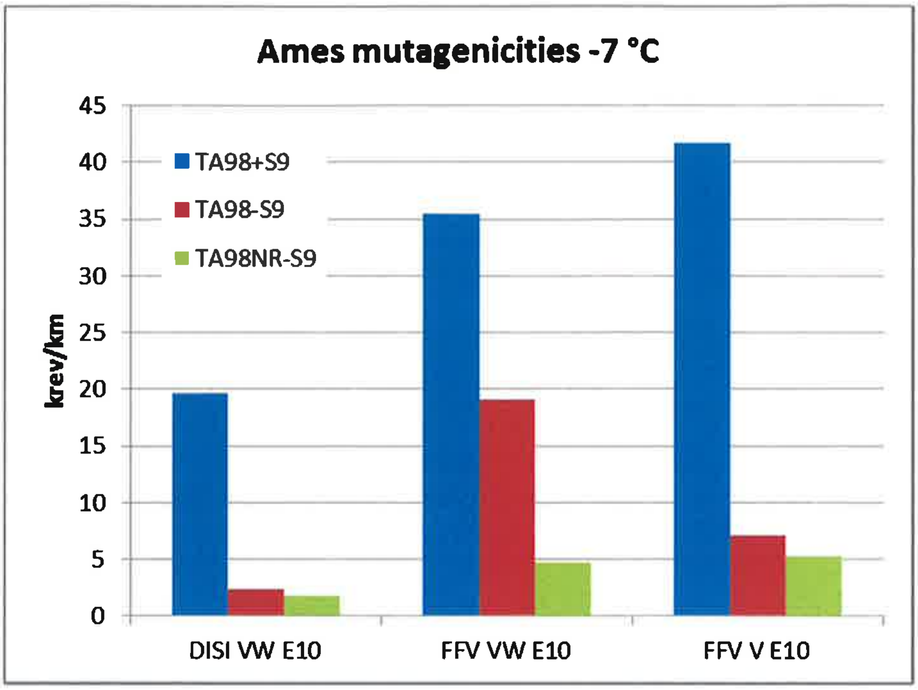



*Figure 15. Mutagenicity of the PM emissions generated by three spark-ignition cars at -7 °C (tester strains TA98+S9, TA98-S9, and TA98NR-S9) with E10.*

## 4. Summary

Unregulated emissions from nine Euro 5 emission level cars were studied over the European exhaust emissions driving cycle at +23 °C and at -7 °C. The cars studied included:

- two MPFI and two DISI gasoline cars using E10 fuel
- two FFV cars using E10 and E85 fuels
- three diesel cars equipped with diesel particulate filter (DPF)

The CO and HC emissions were mostly higher for spark-ignition cars than for diesel cars at both test temperatures, except in one case (diesel 2011 at +23 °). $NO_x$ emissions were higher for diesel cars than those for spark-ignition cars.

Methane and ethene were dominating C1-C8 hydrocarbons for cars using E85 and diesel fuels. For E10, benzene, toluene, and xylenes were dominating C1–C8 hydrocarbons, particularly for the older FFV car at -7 °C. The newer FFV car (2013) emitted less C1–C8 hydrocarbons than the older car (2011) when using E10 at -7 °C. For diesel cars, C1–C8 emissions were generally lower than those for the spark-ignition cars, and this was emphasised at -7 °C. Emission level of 1,3-butadiene was very low for all the cars tested, in maximum 1.9 mg/km.

Aldehyde emissions typically increased for spark-ignition cars when moving from +23 °C to -7 °C. Aldehyde emissions were low for cars using E10, whereas when using E85 high acetaldehyde and ethanol emissions were observed. Formaldehyde emissions were higher for cars using diesel or E85 than for cars using E10 fuels. Aldehyde emissions were lower for newer (2013) than for older diesel cars (2011). Only E85 resulted in higher acetaldehyde emissions than the older diesel car.

Substantial ammonia emissions were observed for spark-ignition cars (induced by the three-way catalyst). Ammonia was not present in the exhaust gas from diesel cars, which were not equipped with SCR (ammonia slip is characteristic for the SCR equipped vehicles).

PM emissions were low, below 4.5 mg/km, for all cars at +23 °C. PM emissions increased up to 14 mg/km when moving from +23 °C to -7 °C. Priority PAH emissions also increased with decreasing test temperature. The highest emissions of PM and priority PAHs were observed for E10 fuelled FFV cars, the second highest for the other cars fuelled with E10 and E85, and the lowest emissions for the DPF equipped diesel cars. Priority PAH emissions were low for MPFI hybrid car when compared with other E10 fuelled cars. According to the Ames tests, at -7 °C the highest indirect mutagenicity (TA98+S9) was exhibited by the E10 fuelled FFV cars in terms of krev/km, which is largely attributable to the higher PM emissions generated by these cars. Also one DISI car showed rather high response in the Ames test. For other cars, the indirect mutagenicity was relatively low. Additional Ames tests were carried out for three cars (E10 fuelled DISI and two FFVs, at -7 °C). These tests indicated a substantially higher role of indirect acting mutagens, such as PAHs, than of direct acting mutagens. In addition, nitro-PAHs seemed to be present in the particles from the older FFV car, but not from the DISI and the newer FFV car.

General trends in emissions when diesel, E10 and E85 are compared with each other are presented in in Table 2 and in Figure 16.

*Table 2. General trends in emissions when diesel, E10 and E85 are compared with each other.*

| | **Lower emissions** | **Higher emissions** |
|---|---|---|
| Diesel w DPF | CO, HC, PM, PAH, $NH_3$ | $NO_X$, formaldehyde |
| Gasoline E10 | $NO_X$, formaldehyde (very low for MPFI hybrid) | CO, HC, PM, PAH, BTEX |
| E85 | $NO_X$ (PM and PAH +23 °C) | CO (-7 °C), HC, methane, acetaldehyde |

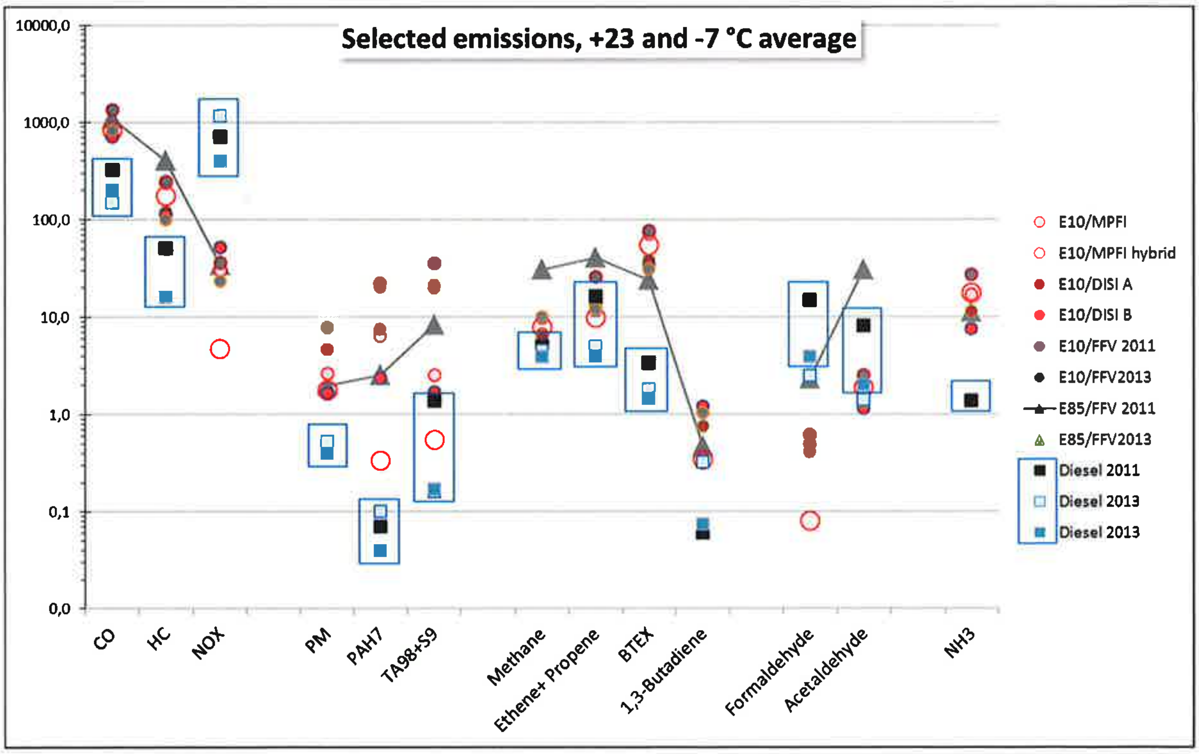



*Figure 16. An overview on the emissions for nine cars tested over the European driving cycle at +23 and -7 °C temperatures. Unit is mg/km for other emissions than PAH7 (µg/km) and Ames TA98+S9 (krev/km).*

# APPENDICES

**Regulated emissions mg/km:**

| +23 °C | CO | HC | $NO_X$ | PM |
|---|---|---|---|---|
| MPFI TA E10 | 249,52 | 49,14 | 13,88 | 1,03 |
| MPFI hybrid TA E10 | 297,43 | 35,74 | 4,14 | 1,43 |
| DISI VW E10 | 306,36 | 21,80 | 13,58 | 2,11 |
| DISI AR E10 | 377,63 | 52,06 | 32,07 | 0,59 |
| FFV VW E10 | 417,41 | 36,19 | 13,48 | 2,54 |
| FFV VW RE85 | 261,71 | 50,57 | 14,66 | 1,20 |
| FFV V E10 | 307,23 | 26,54 | 15,14 | 2,02 |
| FFV V RE85 | 177,30 | 87,64 | 19,17 | 0,54* |
| Diesel VW | 256,34 | 44,87 | 192,19 | 0,40 |
| Diesel V | 108,65 | 13,46 | 439,69 | 0,37 |
| Diesel MB | 193,33 | 14,19 | 183,57 | 0,42 |

**large difference in parallel analyses*

| -7 °C | CO | HC | $NO_X$ | PM |
|---|---|---|---|---|
| MPFI TA E10 | 1312,86 | 425,75 | 46,31 | 4,18 |
| MPFI hybrid TA E10 | 1350,74 | 316,68 | 5,24 | 2,11 |
| DISI VW E10 | 1119,45 | 221,13 | 91,82 | 7,30 |
| DISI AR E10 | 1047,38 | 172,06 | 72,03 | 2,75 |
| FFV VW E10 | 2258,39 | 458,38 | 59,18 | 13,16 |
| FFV VW RE85 | 1922,85 | 749,88 | 54,11 | 2,78 |
| FFV V E10 | 1335,22 | 174,69 | 31,95 | 13,76 |
| FFV V RE85 | n.a. | n.a. | n.a. | n.a. |
| Diesel VW | 389,47 | 55,76 | 1233,30 | 0,47 |
| Diesel V | 193,10 | 18,55 | 1886,76 | 0,68 |
| Diesel MB | 208,32 | 18,12 | 622,62 | 0,38 |

*n.a. = not analyzed*

## C1–C8 emissions mg/km:

| 23 °C | Methane | Ethane | Ethene | Propane | Propene | Acetylene | Isobutene | 1,3-Butadiene | Benzene | Toluene | Ethylbenzene | *m-, p-* Xylene | o-Xylene | BTEX |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **MPFI TA E10** | 4,06 (±1,52) | 0,00 (±0,00) | 2,73 (±0,00) | 0,15 (±0,21) | 1,23 (±0,06) | 0,73 (±0,17) | 0,91 (±0,13) | 0,14 (±0,02) | 1,74 (±0,07) | 5,26 (±0,33) | 0,93 (±1,31) | 1,98 (±2,8) | 0,49 (±0,69) | 10,40 |
| **MPFI hybrid TA E10** | 8,38 (±0,09) | 0,00 (±0,00) | 0,89 (±0,16) | 0,01 (±0,02) | 0,34 (±0,07) | 0,12 (±0,18) | 0,32 (±0,16) | 0,00 (±0,00) | 4,58 (±4,41) | 2,48 (±0,69) | 0,77 (±1,09) | 1,92 (±0,32) | 0,38 (±0,54) | 10,15 |
| **DISI VW E10** | 3,29 (±0,44) | 0,37 (±0,53) | 1,85 (±0,03) | 0,97 (±1,38) | 0,65 (±0,01) | 0,13 (±0,08) | 0,44 (±0,00) | 0,16 (±0,02) | 1,31 (±0,16) | 2,15 (±0,23) | 0,59 (±0,12) | 1,32 (±0,20) | 0,63 (±0,13) | 5,99 |
| **DISI AR E10** | 3,80 (±0,97) | 1,42 (±0,04) | 4,94 (±0,36) | 0,00 (±0,00) | 2,19 (±0,15) | 1,25 (±0,72) | 1,39 (±0,00) | 0,93 (±0,20) | 2,59 (±0,25) | 6,96 (±0,33) | 1,83 (±0,63) | 4,55 (±0,11) | 1,84 (±0,08) | 17,76 |
| **FFV VW E10** | 3,16 (±0,61) | 0,93 (±0,54) | 3,52 (±1,03) | 0,00 (±0,00) | 1,27 (±0,27) | 0,13 (±0,10) | 0,65 (±0,11) | 0,16 (±0,02) | 2,59 (±1,22) | 4,49 (±1,17) | 1,62 (±0,21) | 3,20 (±0,54) | 1,11 (±0,36) | 13,02 |
| **FFV VW RE85** | 15,05 (±1,45) | 2,58 (±0,16) | 7,30 (±1,27) | 0,00 (±0,00) | 0,35 (±0,06) | 0,01 (±0,01) | 0,15 (±0,04) | 0,00 (±0,00) | 0,66 (±0,15) | 0,89 (±0,15) | 1,08 (±0,44) | 1,05 (±0,53) | 0,21 (±0,30) | 3,89 |
| **FFV V E10** | 4,49 (±1,90) | 0,41 (±0,58) | 1,93 (±0,33) | 0,09 (±0,13) | 0,71 (±0,21) | 0,49 (±0,16) | 0,39 (±0,11) | 0,28 (±0,09) | 1,19 (±0,15) | 2,37 (±0,35) | 0,61 (±0,19) | 1,34 (±0,29) | 0,47 (±0,11) | 5,98 |
| **FFV V RE85** | 10,22 (±2,48) | 1,41 (±0,09) | 7,42 (±1,36) | 0,10 (±0,14) | 0,48 (±0,08) | 1,23 (±0,01) | 0,31 (±0,06) | 0,34 (±0,21) | 0,72 (±0,15) | 2,15 (±1,00) | 0,78 (±0,22) | 1,59 (±0,60) | 0,61 (±0,22) | 5,85 |
| **Diesel VW** | 6,45 (±0,25) | 0,00 (±0,00) | 12,73 (±1,44) | 0,00 (±0,00) | 2,31 (±0,56) | 0,06 (±0,01) | 0,21 (±0,08) | 0,12 (±0,06) | 1,42 (±0,17) | 0,40 (±0,25) | 0,77 (±0,2) | 0,80 (±0,39) | 0,18 (±0,25) | 3,55 |
| **Diesel V** | 5,14 (±1,64) | 0,00 (±0,00) | 3,54 (±0,46) | 0,00 (±0,00) | 0,89 (±0,1) | 0,39 (±0,00) | 0,05 (±0,07) | 0,30 (±0,05) | 0,66 (±0,19) | 0,16 (±0,11) | 0,36 (±0,51) | 0,17 (±0,24) | 0,08 (±0,11) | 1,43 |
| **Diesel MB** | 5,19 (±0,02) | 0,00 (±0,00) | 4,28 (±1,80) | 0,00 (±0,00) | 0,68 (±0,28) | 0,09 (±0,13) | 0,00 (±0,00) | 0,15 (±0,02) | 0,54 (±0,16) | 0,16 (±0,02) | 0,48 (±0,02) | 0,42 (±0,07) | 0,00 (±0,00) | 1,60 |

| -7 °C | Methane | Ethane | Ethene | Propane | Propene | Acetylene | Isobutene | 1,3-Butadiene | Benzene | Toluene | Ethylbenzene | *m-, p-* Xylene | o-Xylene | BTEX |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| MPFI TA E10 | 9,22 (±0,27) | 3,12 (±0,01) | 15,62 (±0,45) | 0,24 (±0,04) | 7,79 (±0,22) | 4,73 (±0,51) | 7,22 (±0,32) | 0,54 (±0,07) | 9,36 (±0,47) | 54,51 (±3,41) | 13,26 (±1,5) | 40,24 (±3,46) | 15,38 (±0,56) | 132,74 |
| MPFI hybrid TA E10 | 7,14 (±0,88) | 3,10 (±0,14) | 12,47 (±1,08) | 0,36 (±0,06) | 5,90 (±0,28) | 0,85 (±0,26) | 6,45 (±0,16) | 0,68 (±0,84) | 9,13 (±0,84) | 38,98 (±3,52) | 11,10 (±0,99) | 28,41 (±1,85) | 11,46 (±0,96) | 99,08 |
| DISI VW E10 | 9,52 (±1,66) | 2,69 (±0,38) | 16,01 (±4,54) | 0,00 (±0,00) | 6,54 (±1,86) | 4,67 (±0,46) | 4,82 (±1,28) | 1,35 (±0,18) | 9,24 (±2,53) | 28,41 (±7,30) | 5,97 (±1,59) | 19,09 (±6,74) | 6,92 (±1,32) | 69,63 |
| DISI AR E10 | 6,92 (±0,39) | 2,60 (±0,40) | 11,05 (±0,98) | 0,09 (±0,13) | 5,12 (±0,49) | 3,74 (±0,90) | 3,23 (±0,38) | 1,50 (±0,17) | 5,84 (±0,33) | 20,17 (±0,95) | 5,57 (±0,46) | 13,68 (±0,97) | 5,19 (±0,38) | 50,45 |
| FFV VW E10 | 16,63 (±0,06) | 5,99 (±0,38) | 34,12 (±0,27) | 0,48 (±0,14) | 12,49 (±0,01) | 6,29 (±0,26) | 6,48 (±0,02) | 1,92 (±0,06) | 24,63 (±0,21) | 54,90 (±1,80) | 12,50 (±0,55) | 35,32 (±2,10) | 13,61 (±0,86) | 140,96 |
| FFV VW RE85 | 45,81 (±4,06) | 10,98 (±0,21) | 68,70 (±15,65) | 0,50 (±0,71) | 3,85 (±0,76) | 27,80 (±5,81) | 1,54 (±0,27) | 0,95 (±0,22) | 7,95 (±1,19) | 15,64 (±4,84) | 4,44 (±1,76) | 11,12 (±3,56) | 4,40 (±1,61) | 43,56 |
| FFV V E10 | 15,54 (±0,99) | 2,42 (±0,04) | 15,85 (±0,70) | 6,29 (±8,90) | 5,38 (±0,11) | 7,48 (±0,14) | 3,52 (±0,05) | 1,81 (±0,08) | 11,46 (±0,72) | 21,10 (±0,69) | 5,39 (±0,05) | 13,40 (±0,51) | 4,90 (±0,26) | 56,26 |
| FFV V RE85 | n.a. - | n.a. - | n.a. - | n.a. - | n.a. - | n.a. - | n.a. - | n.a. - | n.a. - | n.a. - | n.a. - | n.a. - | n.a. - | n.a. |
| Diesel VW | 3,52 (±1,22) | 0,00 (±0,00) | 15,51 (±1,44) | 0,00 (±0,00) | 2,43 (±0,36) | 0,61 (±0,35) | 0,27 (±0,12) | 0,00 (±0,00) | 1,56 (±0,24) | 0,67 (±0,08) | 0,23 (±0,32) | 0,48 (±0,68) | 0,23 (±0,32) | 3,16 |
| Diesel V | 3,89 (±0,11) | 0,00 (±0,00) | 4,84 (±0,48) | 0,20 (±0,29) | 0,66 (±0,10) | 1,22 (±0,08) | 0,17 (±0,06) | 0,35 (±0,11) | 1,08 (±0,01) | 0,70 (±0,17) | 0,28 (±0,39) | 0,12 (±0,17) | 0,00 (±0,00) | 2,18 |
| Diesel MB | 2,61 (±1,66) | 0,00 (±0,00) | 2,58 (±3,65) | 0,00 (±0,00) | 0,39 (±0,56) | 0,17 (±0,26) | 0,00 (±0,00) | 0,00 (±0,00) | 0,46 (±0,46) | 0,30 (±0,21) | 0,37 (±0,52) | 0,18 (±0,26) | 0,00 (±0,00) | 1,31 |

*n.a. = not analyzed;BTEX = Benzene + Toluene + Ethylbenzene + Xylenes*

**Aldehyde emissions mg/km:**

| +23 °C | FA | AA | Acro | PrA | CrA | MeCr | BuA | BzA | VA | mTol | HexA | SUM |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| MPFI TA E10 | 0,36 (±0,14) | 0,72 (±0,27) | 0,05 (±0,02) | 0,03 (±0,01) | 0,00 (±0,00) | 0,03 (±0,01) | 0,00 (±0,00) | 0,06 (±0,03) | 0,00 (±0,00) | 0,00 (±0,00) | 0,00 (±0,00) | 1.3 |
| MPFI TA hybrid E10 | 0,09 (±0,08) | 0,38 (±0,04) | 0,02 (±0,00) | 0,01 (±0,00) | 0,00 (±0,00) | 0,01 (±0,01) | 0,00 (±0,00) | 0,04 (±0,05) | 0,00 (±0,00) | 0,00 (±0,00) | 0,00 (±0,00) | 0,6 |
| DISI VW E10 | 0,22 (±0,04) | 0,31 (±0,03) | 0,02 (±0,00) | 0,03 (±0,01) | 0,00 (±0,00) | 0,02 (±0,00) | 0,00 (±0,00) | 0,07 (±0,02) | 0,00 (±0,00) | 0,00 (±0,00) | 0,00 (±0,00) | 0,7 |
| DISI AR E10 | 0,38 (±0,13) | 0,56 (±0,03) | 0,05 (±0,01) | 0,04 (±0,02) | 0,00 (±0,00) | 0,04 (±0,00) | 0,00 (±0,00) | 0,18 (±0,09) | 0,00 (±0,00) | 0,00 (±0,00) | 0,00 (±0,00) | 1.3 |
| FFV VW E10 | 0,44 (±0,07) | 0,78 (±0,01) | 0,01 (±0,02) | 0,08 (±0,00) | 0,00 (±0,00) | 0,02 (±0,02) | 0,00 (±0,00) | 0,67 (±0,64) | 0,00 (±0,00) | 0,00 (±0,00) | 0,00 (±0,00) | 2.0 |
| FFV VW RE85 | 1,08 (±0,22) | 8,02 (±0,93) | 0,04 (±0,00) | 0,09 (±0,05) | 0,00 (±0,00) | 0,03 (±0,01) | 0,00 (±0,00) | 1,07 (±0,60) | 0,00 (±0,00) | 0,00 (±0,00) | 0,00 (±0,00) | 10.3 |
| FFV V E10 | 0,45 (±0,06) | 0,59 (±0,06) | 0,02 (±0,03) | 0,01 (±0,01) | 0,00 (±0,00) | 0,02 (±0,00) | 0,00 (±0,00) | 0,10 (±0,00) | 0,02 (±0,01) | 0,00 (±0,00) | 0,00 (±0,00) | 1.2 |
| FFV V RE85 | 1,78 (±0,37) | 20,40 (±10,94) | 0,22 (±0,07) | 0,07 (±0,03) | 0,02 0,02 | 0,03 (±0,02) | 0,00 (±0,00) | 0,10 (±0,08) | 0,01 (±0,01) | 0,00 (±0,00) | 0,00 (±0,00) | 22.6 |
| Diesel VW | 13,33 (±1,89) | 7,14 (±0,78) | 1,55 (±0,33) | 0,99 (±0,17) | 0,22 0,07 | 0,33 (±0,01) | 0,25 (±0,06) | 0,16 (±0,14) | 0,08 (±0,06) | 0,00 (±0,00) | 0,00 (±0,00) | 24.1 |
| Diesel V | 1,23 (±0,2) | 0,97 (±0,02) | 0,02 (±0,01) | 0,23 (±0,04) | 0,00 (±0,00) | 0,00 (±0,00) | 0,00 (±0,00) | 0,15 (±0,01) | 0,00 (±0,00) | 0,00 (±0,00) | 0,00 (±0,00) | 2.6 |
| Diesel MB | 2,54 (±0,97) | 1,25 (±0,45) | 0,08 (±0,04) | 0,16 (±0,04) | 0,00 (±0,00) | 0,00 (±0,00) | 0,00 (±0,00) | 0,13 (±0,08) | 0,00 (±0,00) | 0,00 (±0,00) | 0,00 (±0,00) | 4.2 |

| -7 °C | FA | AA | Acro | PrA | CrA | MeCr | BuA | BzA | VA | mTol | HexA | SUM Others |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| MPFI TA E10 | 0,64 (±0,10) | 2,68 (±0,34) | 0,09 (±0,01) | 0,12 (±0,00) | 0,00 (±0,00) | 0,05 (±0,07) | 0,00 (±0,00) | 0,28 (±0,00) | 0,00 (±0,00) | 0,00 (±0,00) | 0,00 (±0,00) | 3.9 |
| MPFI TA hybrid E10 | 0,07 (±0,02) | 3,35 (±0,03) | 0,01 (±0,02) | 0,13 (±0,01) | 0,00 (±0,00) | 0,04 (±0,00) | 0,04 0,015887 | 0,02 (±0,03) | 0,00 (±0,00) | 0,00 (±0,00) | 0,00 (±0,00) | 3.7 |
| DISI VW E10 | 0,60 (±0,06) | 2,12 (±0,55) | 0,09 (±0,01) | 0,09 (±0,03) | 0,00 (±0,00) | 0,10 (±0,02) | 0,00 (±0,00) | 0,14 (±0,04) | 0,00 (±0,00) | 0,00 (±0,00) | 0,00 (±0,00) | 3.1 |
| DISI AR E10 | 0,84 (±0,04) | 1,75 (±0,03) | 0,14 (±0,01) | 0,09 (±0,01) | 0,00 (±0,00) | 0,13 (±0,01) | 0,00 (±0,00) | 0,21 (±0,07) | 0,00 (±0,00) | 0,00 (±0,00) | 0,00 (±0,00) | 3.2 |
| FFV VW E10 | 0,78 (±0,03) | 4,27 (±0,11) | 0,08 (±0,00) | 0,20 (±0,03) | 0,00 (±0,00) | 0,10 (±0,00) | 0,00 (±0,00) | 0,34 (±0,01) | 0,00 (±0,00) | 0,00 (±0,00) | 0,00 (±0,00) | 5.8 |
| FFV VW RE85 | 3,50 (±0,41) | 52,58 (±12,05) | 0,28 (±0,04) | 0,57 (±0,10) | 0,96 (±0,05) | 0,29 (±0,01) | 0,08 (±0,11) | 0,70 (±0,26) | 0,00 (±0,00) | 0,00 (±0,00) | 0,00 (±0,00) | 59.0 |
| FFV V E10 | 0,58 (±0,17) | 2,04 (±0,05) | 0,06 (±0,01) | 0,05 (±0,02) | 0,00 (±0,00) | 0,06 (±0,01) | 0,01 (±0,00) | 0,20 (±0,02) | 0,02 (±0,03) | 0,02 (±0,00) | 0,00 (±0,00) | 3.0 |
| FFV V RE85 | n.a. - | n.a. - | n.a. - | n.a. - | n.a. - | n.a. - | n.a. - | n.a. - | n.a. - | n.a. - | n.a. - | n.a. |
| Diesel VW | 16,45 (±4,88) | 9,19 (±2,05) | 2,11 (±0,48) | 1,17 (±0,31) | 0,26 (±0,13) | 0,42 (±0,11) | 0,38 (±0,10) | 0,69 (±0,25) | 0,10 (±0,14) | 0,00 (±0,00) | 0,00 (±0,00) | 30.8 |
| Diesel V | 3,77 (±1,32) | 1,84 (±0,68) | 0,15 (±0,04) | 0,18 (±0,03) | 0,00 (±0,00) | 0,00 (±0,00) | 0,00 (±0,00) | 0,08 (±0,02) | 0,02 (±0,00) | 0,00 (±0,00) | 0,00 (±0,00) | 6.0 |
| Diesel MB | 5,22 (±0,85) | 2,79 (±0,35) | 0,45 (±0,09) | 0,44 (±0,06) | 0,00 (±0,00) | 0,03 (±0,00 | 0,01 (±0,00 | 0,16 (±0,06) | 0,00 (±0,00) | 0,00 (±0,00) | 0,00 (±0,00) | 9.1 |

*n.a. = not analysed;FA = Formaldehyde, AA = Acetaldehyde, Acro = Acrolein, PrA = Propionaldehyde, CrA = Crotonaldehyde, MeCr = Methacrolein, BuA = Butyraldehyde, Bz = Benazaldehyde, VA = Valeradehyde, mTol = m-tolualdehyde, and HexA = Hexanal*

*FTIR*

| +23 °C | | $N_2O$ (mg/km) | $NH_3$ (mg/km) | Ethanol (mg/km) |
|---|---|---|---|---|
| MPFI TA E10 | E10 | 6,02 | 10,01 | - |
| | | 6,05 | 8,21 | - |
| | **Average** | **6,03** | **9,11** | **-** |
| | **STDEV** | **0,02** | **1,27** | **-** |
| MPFI hybrid TA E10 | E10 | 3,38 | 17,42 | - |
| | | 4,06 | 19,98 | - |
| | **Average** | **3,72** | **18,70** | **-** |
| | **STDEV** | **0,48** | **1,81** | **-** |
| DISI VW E10 | E10 | 4,35 | 3,29 | - |
| | | 4,04 | 8,49 | - |
| | **Average** | **4,19** | **5,89** | **-** |
| | **STDEV** | **0,22** | **3,68** | **-** |
| DISI AR E10 | E10 | 5,79 | 8,27 | - |
| | | 5,99 | 5,19 | - |
| | **Average** | **5,89** | **6,73** | **-** |
| | **STDEV** | **0,14** | **2,18** | **-** |
| FFV VW E10 | E10 | 3,72 | 6,83 | 2,31 |
| | | 1,59 | 7,48 | 3,01 |
| | **Average** | **2,65** | **7,15** | **2,66** |
| | **STDEV** | **1,51** | **0,46** | **0,49** |
| FFV VW E85 | E85 | 7,30 | 5,70 | 29,52 |
| | | 3,07 | 4,24 | 22,30 |
| | **Average** | **5,19** | **4,97** | **25,91** |
| | **STDEV** | **2,98** | **1,03** | **5,11** |
| Diesel VW | Diesel | 8,31 | 1,31 | - |
| | | 7,31 | 1,18 | - |
| | **Average** | **7,81** | **1,24** | **-** |
| | **STDEV** | 0,71 | 0,09 | - |

| -7 °C | | $N_2O$ (mg/km) | $NH_3$ (mg/km) | Ethanol (mg/km) |
|---|---|---|---|---|
| MPFI TA E10 | E10 | 7,00 | 23,73 | - |
| | | 7,79 | 25,42 | - |
| | **Average** | **7,40** | **24,57** | **-** |
| | **STDEV** | **0,56** | **1,19** | **-** |
| MPFI hybrid TA E10 | E10 | 5,23 | 18,56 | - |
| | | 4,81 | 14,32 | - |
| | **Average** | **5,02** | **16,44** | **-** |
| | **STDEV** | **0,30** | **3,00** | **-** |
| DISI VW E10 | E10 | 7,51 | 11,42 | - |
| | | 5,07 | 22,74 | - |
| | **Average** | **6,29** | **17,08** | **-** |
| | **STDEV** | **1,73** | **8,01** | **-** |
| DISI AR E10 | E10 | 8,97 | 7,49 | - |
| | | 8,87 | 9,40 | - |
| | **Average** | **8,92** | **8,45** | **-** |
| | **STDEV** | **0,07** | **1,35** | **-** |
| FFV VW E10 | E10 | 5,17 | 43,66 | 29,24 |
| | | 2,51 | 50,03 | 32,53 |
| | **Average** | **3,84** | **46,84** | **30,89** |
| | **STDEV** | **1,88** | **4,50** | **2,33** |
| FFV VW E85 | E85 | 2,37 | 18,35 | 1049,37 |
| | | 2,11 | 16,32 | 573,67 |
| | **Average** | **2,24** | **17,33** | **811,52** |
| | **STDEV** | **0,18** | **1,44** | **336,37** |
| Diesel VW | Diesel | 14,74 | 1,43 | - |
| | | 13,93 | 1,59 | - |
| | **Average** | **14,34** | **1,51** | **-** |
| | **STDEV** | **0,57** | **0,11** | - |

**PAH emissions µg/km:**

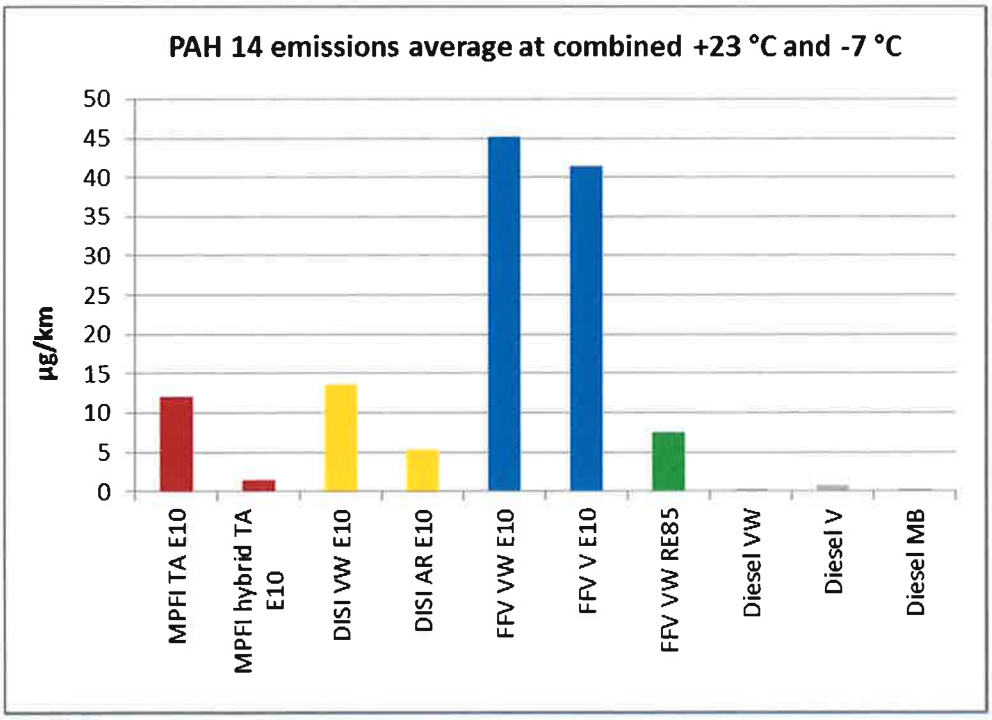
| +23 °C | MPFI TA E10 | MPFI hybrid TA E10 | DISI VW E10 | DISI AR E10 | FFV VW E10 | FFV VW RE85 | FFV V E10 | FFV V RE85 | Diesel V +23 & -7 °C | Diesel VW +23 & -7 °C | Diesel MB +23 & -7 °C |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Naphtalene | 0,03 | 0,06 | 0,57 | 0,05 | 0,26 | 0,03 | 0,12 | 0,28 | 0,03 | 0,01 | 0,04 |
| 2-Methylnaphthalene | 0,09 | 0,16 | 0,20 | 0,05 | 0,31 | 0,10 | 0,06 | 0,18 | 0,03 | 0,04 | 0,03 |
| 1-Methylnaphthalene | 0,03 | 0,03 | 0,05 | 0,02 | 0,10 | 0,04 | 0,02 | 0,05 | 0,01 | 0,02 | 0,01 |
| 1,1-Biphenyl | 0,04 | 0,17 | 0,26 | 0,03 | 0,44 | 0,06 | 0,03 | 0,03 | 0,04 | 0,04 | 0,02 |
| Acenaphthylene | 0,05 | 0,01 | 0,06 | 0,01 | 0,08 | 0,01 | 0,06 | 0,05 | 0,01 | 0,01 | 0,00 |
| Acenaphthene | 0,00 | 0,00 | 0,01 | 0,00 | 0,03 | 0,01 | 0,01 | 0,03 | 0,05 | 0,00 | 0,07 |
| Dibenzofurane | 0,02 | 0,05 | 0,08 | 0,01 | 0,26 | 0,04 | 0,05 | 0,02 | 0,01 | 0,05 | 0,01 |
| Fluorene | 0,04 | 0,04 | 0,08 | 0,01 | 0,22 | 0,05 | 0,03 | 0,02 | 0,00 | 0,02 | 0,01 |
| Dibenzothiophene | 0,00 | 0,02 | 0,01 | 0,00 | 0,02 | 0,02 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 |
| Phenanthrene | 0,24 | 0,16 | 0,29 | 0,10 | 0,27 | 0,08 | 0,41 | 0,16 | 0,07 | 0,03 | 0,03 |
| Anthracene | 0,05 | 0,03 | 0,07 | 0,02 | 0,08 | 0,01 | 0,09 | 0,03 | 0,01 | 0,00 | 0,00 |
| 2-Methylanthracene | 0,03 | 0,02 | 0,03 | 0,01 | 0,04 | 0,01 | 0,06 | 0,02 | 0,02 | 0,00 | 0,01 |
| 1-Methylanthracene | 0,06 | 0,04 | 0,05 | 0,02 | 0,04 | 0,02 | 0,04 | 0,01 | 0,01 | 0,01 | 0,01 |
| 2-phenylnaphthalene | 0,10 | 0,07 | 0,12 | 0,05 | 0,10 | 0,04 | 0,14 | 0,05 | 0,04 | 0,01 | 0,02 |
| Fluoranthene | 0,56 | 0,34 | 0,64 | 0,31 | 0,59 | 0,32 | 0,62 | 0,29 | 0,24 | 0,07 | 0,13 |
| Pyrene | 1,22 | 0,68 | 1,31 | 0,66 | 1,08 | 0,56 | 0,58 | 0,28 | 0,26 | 0,16 | 0,16 |
| Benzo[*b*]fluorene | 0,18 | 0,08 | 0,15 | 0,06 | 0,15 | 0,06 | 0,14 | 0,01 | 0,01 | 0,03 | 0,01 |
| Benzo[*a*]anthracene | 0,21 | 0,06 | 0,15 | 0,07 | 0,20 | 0,08 | 0,20 | 0,01 | 0,02 | 0,03 | 0,01 |
| Chrysene | 0,14 | 0,05 | 0,10 | 0,05 | 0,14 | 0,06 | 0,20 | 0,02 | 0,03 | 0,02 | 0,02 |
| Benzo[*b*]fluoranthene | 0,20 | 0,02 | 0,19 | 0,05 | 0,28 | 0,03 | 0,23 | 0,01 | 0,02 | 0,01 | 0,01 |
| Benzo[*k*]fluoranthene | 0,04 | 0,01 | 0,04 | 0,02 | 0,08 | 0,01 | 0,14 | 0,01 | 0,01 | 0,00 | 0,00 |
| Benzo(*j*)fluoranthene | 0,02 | 0,00 | 0,04 | 0,01 | 0,05 | 0,00 | 0,13 | 0,00 | 0,01 | 0,00 | 0,00 |
| 7,12-Dimethylbenz[*a*]anthracene | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 |
| Benzo[e]pyrene | 0,11 | 0,01 | 0,08 | 0,03 | 0,13 | 0,02 | 0,16 | 0,02 | 0,01 | 0,01 | 0,00 |
| Benzo[*a*]pyrene | 0,10 | 0,01 | 0,14 | 0,04 | 0,22 | 0,02 | 0,27 | 0,02 | 0,02 | 0,00 | 0,01 |
| Perylene | 0,02 | 0,00 | 0,02 | 0,01 | 0,04 | 0,00 | 0,08 | 0,00 | 0,00 | 0,00 | 0,00 |
| Indeno[1,2,3-*cd*]pyrene | 0,00 | 0,00 | 0,08 | 0,03 | 0,16 | 0,00 | 0,28 | 0,02 | 0,01 | 0,00 | 0,00 |
| Dibenzo[*a,h*]anthracene | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 0,24 | 0,06 | 0,02 | 0,00 | 0,00 |
| Benzo[*g,h,i*]perylene | 0,09 | 0,00 | 0,10 | 0,04 | 0,16 | 0,03 | 0,02 | 0,00 | 0,00 | 0,00 | 0,00 |
| Coronene | 0,00 | 0,00 | 0,05 | 0,00 | 0,07 | 0,00 | 0,11 | 0,04 | 0,01 | 0,00 | 0,00 |
| Benzo[*a*]fluorene | 0,15 | 0,07 | 0,15 | 0,06 | 0,16 | 0,07 | n.a. | n.a. | n.a. | 0,02 | n.a. |
| Total PAH | 3,8 | 2,2 | 5,1 | 1,8 | 5,8 | 1,8 | 4,5 | 1,7 | 1,0 | 0,6 | 0,6 |
| PAH 14 | 3,01 | 1,40 | 3,27 | 1,41 | 3,60 | 1,28 | 3,48 | 0,95 | 0,73 | 0,37 | 0,37 |
| PAH 7 | **0,70** | **0,14** | **0,70** | **0,26** | **1,09** | **0,21** | **1,32** | **0,10** | **0,10** | **0,07** | **0,04** |

*n.a. = not analyzed*

| -7 °C | MPFI TA E10 | MPFI hybrid TA E10 | DISI VW E10 | DISI AR E10 | FFV VW E10 | FFV VW RE85 | FFV V E10 | Diesel V +23 & -7 °C | Diesel VW +23 & -7 °C | Diesel MB +23 & -7 °C |
|---|---|---|---|---|---|---|---|---|---|---|
| Naphtalene | 0,13 | 0,35 | 0,66 | 0,16 | 0,52 | 0,13 | 1,52 | 0,03 | 0,01 | 0,04 |
| 2-Methylnaphthalene | 0,23 | 1,44 | 0,73 | 0,10 | 0,71 | 0,35 | 0,74 | 0,03 | 0,04 | 0,03 |
| 1-Methylnaphthalene | 0,08 | 0,35 | 0,15 | 0,03 | 0,17 | 0,09 | 0,17 | 0,01 | 0,02 | 0,01 |
| 1,1-Biphenyl | 0,10 | 0,93 | 1,09 | 0,09 | 2,11 | 0,30 | 1,04 | 0,04 | 0,04 | 0,02 |
| Acenaphthylene | 0,22 | 0,08 | 0,81 | 0,06 | 0,51 | 0,45 | 1,00 | 0,01 | 0,01 | 0,00 |
| Acenaphthene | 0,05 | 0,12 | 0,29 | 0,02 | 0,16 | 0,19 | 0,35 | 0,05 | 0,00 | 0,07 |
| Dibenzofurane | 0,04 | 0,30 | 0,17 | 0,02 | 0,52 | 0,09 | 0,50 | 0,01 | 0,05 | 0,01 |
| Fluorene | 0,11 | 0,05 | 0,09 | 0,02 | 0,51 | 0,14 | 0,14 | 0,00 | 0,02 | 0,01 |
| Dibenzothiophene | 0,00 | 0,00 | 0,00 | 0,00 | 0,04 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 |
| Phenanthrene | 1,43 | 0,12 | 1,00 | 0,36 | 6,33 | 0,38 | 4,56 | 0,07 | 0,03 | 0,03 |
| Anthracene | 0,19 | 0,01 | 0,15 | 0,08 | 0,68 | 0,04 | 1,17 | 0,01 | 0,00 | 0,00 |
| 2-Methylanthracene | 0,12 | 0,01 | 0,06 | 0,02 | 0,25 | 0,02 | 0,51 | 0,02 | 0,00 | 0,01 |
| 1-Methylanthracene | 0,18 | 0,02 | 0,07 | 0,04 | 0,42 | 0,03 | 0,25 | 0,01 | 0,01 | 0,01 |
| 2-phenylnaphthalene | 0,33 | 0,04 | 0,22 | 0,10 | 1,74 | 0,06 | 1,46 | 0,04 | 0,01 | 0,02 |
| Fluoranthene | 1,31 | 0,17 | 1,51 | 0,89 | 7,78 | 1,03 | 10,88 | 0,24 | 0,07 | 0,13 |
| Pyrene | 2,70 | 0,35 | 2,96 | 1,96 | 14,52 | 3,01 | 10,22 | 0,26 | 0,16 | 0,16 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Benzo[*b*]fluorene | 1,50 | 0,06 | 1,23 | 0,39 | 3,79 | 0,36 | 1,67 | 0,01 | 0,03 | 0,01 |
| **Benzo[*a*]anthracene** | 2,11 | 0,09 | 2,24 | 0,71 | 7,12 | 0,55 | 5,86 | 0,02 | 0,03 | 0,01 |
| **Chrysene** | 1,16 | 0,06 | 1,48 | 0,64 | 4,99 | 0,35 | 5,65 | 0,03 | 0,02 | 0,02 |
| **Benzo[*b*]fluoranthene** | 3,19 | 0,15 | 3,93 | 0,97 | 11,92 | 1,00 | 6,08 | 0,02 | 0,01 | 0,01 |
| **Benzo[*k*]fluoranthene** | 1,02 | 0,04 | 1,19 | 0,44 | 3,36 | 0,40 | 4,26 | 0,01 | 0,00 | 0,00 |
| Benzo(*j*)fluoranthene | 0,73 | 0,04 | 0,86 | 0,31 | 2,02 | 0,12 | 3,87 | 0,01 | 0,00 | 0,00 |
| **7,12-Dimethylbenz[*a*]anthracene** | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 |
| Benzo[e]pyrene | 1,57 | 0,07 | 1,54 | 0,50 | 4,86 | 1,05 | 4,34 | 0,01 | 0,01 | 0,00 |
| **Benzo[*a*]pyrene** | 3,19 | 0,12 | 3,59 | 1,27 | 9,06 | 1,56 | 9,55 | 0,02 | 0,00 | 0,01 |
| Perylene | 0,67 | 0,03 | 0,80 | 0,23 | 2,01 | 0,24 | 2,45 | 0,00 | 0,00 | 0,00 |
| **Indeno[1,2,3-*cd*]pyrene** | 1,31 | 0,07 | 1,85 | 0,50 | 6,88 | 0,95 | 7,81 | 0,01 | 0,00 | 0,00 |
| Dibenzo[*a,h*]anthracene | 0,16 | 0,00 | 0,33 | 0,16 | 0,77 | 0,10 | 8,22 | 0,02 | 0,00 | 0,00 |
| Benzo[*g,h,i*]perylene | 1,55 | 0,12 | 2,37 | 0,71 | 7,97 | 3,05 | 0,54 | 0,00 | 0,00 | 0,00 |
| Coronene | 0,70 | 0,08 | 1,52 | 0,47 | 4,15 | 1,41 | 4,34 | 0,01 | 0,00 | 0,00 |
| Benzo[*a*]fluorene | 1,23 | 0,06 | 1,19 | 0,35 | 3,50 | 0,27 | n.a. | n.a. | 0,02 | n.a. |
| **Total PAH** | **27,3** | **5,4** | **34,1** | **11,6** | **109,4** | **17,7** | **99,2** | **1,0** | **0,6** | **0,6** |
| **PAH 14** | **20,99** | **1,43** | **24,22** | **9,20** | **86,76** | **13,59** | **79,28** | **0,73** | **0,37** | **0,37** |
| **PAH 7** | **11,98** | **0,53** | **14,28** | **4,52** | **43,34** | **4,80** | **39,20** | **0,10** | **0,07** | **0,04** |

*n.a. = not analyzed*
FFV V RE85 not analyzed



**Ames mutagenicity:**

| | TA98+S9, krev/km | | | TA98-S9 krev/km | TA98NR-S9 krev/km |
|---|---|---|---|---|---|
| | +23 °C | -7 °C | +23 °C and -7 °C combined | -7 °C | -7 °C |
| **MPFI TA E10** | - | 2,53 | - | - | - |
| **MPFI hybrid TA E10** | - | 0,55 | - | - | - |
| **DISI VW E10** | - | 19,67 | - | 2,37 | 1,79 |
| **DISI AR E10** | - | 1,69 | - | - | - |
| **FFV VW E10** | - | 35,45 | - | 19,05 | 4,76 |
| **FFV VW RE85** | - | 8,23 | - | - | - |
| **FFV V E10** | 0,79 | 41,64* | - | 7,06* | 5,31* |
| **FFV V RE85** | 0,14 | - | - | - | - |
| **Diesel VW** | - | - | 1,38 | - | - |
| **Diesel V** | - | - | 0,16 | - | - |
| **Diesel MB** | - | - | 0,17 | - | - |

**Average results from two parallel samples*

| | Temp. °C | Krev per mg PM | | |
|---|---|---|---|---|
| | | **TA98+S9** | **TA98-S9** | **TA98NR-S9** |
| **MPFI TA E10** | -7 | 0,60 | - | - |
| **MPFI hybrid TA E10** | -7 | 0,26 | - | - |
| **DISI AR E10** | -7 | 0,63 | - | - |
| **DISI VW E10** | -7 | 2,69 | 0,32 | 0,24 |
| **FFV VW E10** | -7 | 2,69 | 1,44 | 0,36 |
| **FFV VW RE85** | -7 | 2,94 | - | - |
| **FFV V E10** | 23 | 0,40 | - | - |
| **FFV V E10** | -7 | 3,03* | 0,51* | 0,39* |
| **FFV V RE85** | 23 | 0,28 | - | - |
| **Diesel VW** | 23 & -7 | 3,46 | - | - |
| **Diesel V** | 23 & -7 | 0,32 | - | - |
| **Diesel MB** | 23 & -7 | 0,41 | - | - |

**Average results from two parallel samples*