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Effect of Biodiesel Fuels on Pollutant Emissions from EURO 3 LD Diesel Vehicles (1)

Prepared by
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With collaborations from:
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Institute for Environment and Sustainability

2007

EUR 22745 EN

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European Commission
Directorate-General Joint Research Centre
Institute for Environment and Sustainability

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http://ies.jrc.cec.eu.int
http://www.jrc.cec.eu.int

EUR 22745 EN
ISBN 978-92-79-05536-2
ISSN 1018-5593
Luxembourg: Office for Official Publications of the European Communities

Printed in Italy

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Study Jointly Performed by:
Transport and Air Quality Unit; Institute for Environment and Sustainability, EC-Joint Research Centre (Ispra, Italy) and The European Biodiesel Board.

Authors:
This Report has been prepared by: G. Martini, C. Astorga and A. Farfaletti with collaborations from: M. Botta, M. Rey, U. Manfredi, A. Krasenbrink, B. R. Larsen and G. De Santi

Acknowledgement

This experimental programme has been carried out with the essential contribution of: R. Colombo, G. Lanappe, M. Sculati, P. Le Lijour, M. Duane, Anne Mueller. We also acknowledge the contribution of the European Biodiesel Board and in particular of L. Amatruda for having provided the test fuels, the test vehicles and for having reviewed the final report.

Effect of Biodiesel Fuels on Pollutant Emissions from LD Diesel Vehicles (1)

Index

List of Special Terms and Abbreviations

ACN	Acetonitrile
APCI	Atmospheric pressure chemical ionization
BaP	Benzo(a)pyrene
CEPA	California Environmental Protection Agency
CI	Chemical ionisation
CFPP	Cold Filter Plugging Point
CVS	Constant Volume Sampler
DG	Direction General
DI	Direct Injection
ECE15	European Urban Driving Cycle
EGR	Exhaust Gas Recirculation
EHU	Emissions and Health Unit
EI	Electron impact
EOI	End of Injection
EPA	US-Environmental Protection Agency
EC	European Commission
EMS	Engine Management System
ESC	European Stationary Cycle (Heavy Duty)
EU	European Union
EUDC	Extra Urban Driving Cycle
FID	Flame ionization detector
GC	Gas chromatography
GC-MS	Gas chromatography mass spectrometry

HD	Heavy Duty
HPLC	High performance liquid chromatography
IARC	International agency for research on cancer
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
i. d.	Inner Diameter
IDI	Indirect Injection
IES	Institute of Environment and Sustainability
IPCS	The international programme on chemical safety
IR	Infrared red spectroscopy
JRC	Joint Research Centre
LC-MS	Liquid chromatography mass spectrometry
LD	Light Duty
LPI	Low Pressure Impactor
LRC	Large Reservoir Capacity
MS	Mass spectrometry.
MoU	Memorandum of Understanding
m/z	Mass to charge ratio for detected ions in mass spectrometry
NCI	Negative chemical ionisation.
NEDC	New European Driving Cycle
Nitro-PAH	Nitro substituted polyaromatic hydrocarbon
O-PAC	Oxygen analogues of polyaromatic hydrocarbon
PAC	Polyaromatic compounds
PAH	Polyaromatic hydrocarbon
PC	Passenger Car
PCI	Positive chemical ionisation
PM	Particulate Matter

PRS	Propylsulfonicacid solid phase extraction column
psi	Pound per square inch, 1 psi = 6896 N/m^2
PTFE	Polytetrafluoroethylene, Teflon®
PUF	Polyurethane foam
Ramp #	Number of rate used in the temperature program in GC
RF	Response factor
ROG	Reactive Organic Gases
RPLC	Reverse phase liquid chromatography
RSD	Relative standard deviation, the standard deviation of a sample divided by the sample mean
Scan mode	When operated in the scan mode the MSD collects data by scanning and detecting through a range of ions
SIM mode	Single ion monitoring, only selected ions are monitored
SOF	Soluble Organic Fraction
SOI	Start of Injection
SPE	Solid phase extraction
Split mode	The carrier gas flow through a point of split, is divided so only a fraction continues through the system the main part is vented out
Splitless mode	For a given period of time there is no division of carrier flow at the split point. After the period the system returns to split mode
TEA	Triethylamine
TEF	Toxicity Equivalence Factor
TEQ	Toxicity Equivalence
TIC	Total Ion Current chromatogram. The plots of the accumulated signals from all the ions in the selected m/z scan range versus time. A chromatogram generated by operating the MSD in the scan mode
Torr	1 Torr = 133.322 N/m^2
VELA	Vehicles Emission Laboratory
WCOT	Wall Coated Open Tubular column, a type of capillary column

ABSTRACT

Transport is a key factor in modern economies. However, the EU transport system is currently not sustainable, and in many respects moving away from sustainability rather than towards it. The European Environment Agency highlights in particular the sector's growing CO2 emissions that threaten the EU meeting its target under the Kyoto protocol. Transport also represents a key challenge to sustainability in terms of depletion of resources and European competitiveness, safety and security concerns, especially due to the monolithic reliance on a single energy source.

As stated in the Commission's November 2000 Green Paper on security of supply, in 1998 energy consumption in the transport sector was to blame for 28 % of emissions of CO2, the leading greenhouse gas. In particular, road transport alone accounts for 84 % of the CO2 emissions attributable to transport.

Furthermore, in terms of security of energy supply, there is growing concern for the current situation of transport sector that depends on crude oil for more than 99%.

In the above mentioned Green Paper the European Commission has also identified the measures to tackle these problems and, among them, one the most important is the promotion of alternative fuels; the ambitious target that has been proposed by the Commission is to replace 20% of conventional fuels with substitute fuels by 2020.

According to the Commission White Paper "European transport policy for 2010: time to decide" the most promising forms are biofuels in the short and medium term, natural gas in the medium and long term and hydrogen in the very long term.

On the basis of the above mentioned Papers, in 2003 the European Union has adopted two Directives, the EC/2003/30 and the EC/2003/96, with the overall objective of promoting the use of biofuels. The first Directive set the targets for market share of biofuels for 2005 (2% in terms of energy content) and 2010 (5.75%); the second Directive set the framework for tax incentives for the promotion of biofuels.

Biodiesel is currently the most produced biofuel in Europe: the production in 2003 was about of 1500000 (EU25) tons with an increase of more than 32% compared to the 2002 figure.

Within this policy framework, the Joint Research Centre and the European Biodiesel Board have decided to cooperate to investigate the effect of biodiesel on pollutant emissions from diesel engines. In particular, in this report the effect of biodiesel fuels produced from different raw materials on the regulated emissions from light duty diesel vehicles are compared to the effect on other regulated and unregulated pollutants.

EFFECT OF BIODIESEL FUELS ON POLLUTANT EMISSIONS FROM LD DIESEL VEHICLES

1 Summary

Transport is a key factor in modern economies. However, the EU transport system is currently not sustainable, and in many respects moving away from sustainability rather than towards it. The European Environment Agency highlights in particular the sector's growing CO2 emissions that threaten the EU meeting its target under the Kyoto protocol. Transport also represents a key challenge to sustainability in terms of depletion of resources and European competitiveness, safety and security concerns, especially due to the monolithic reliance on a single energy source.
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Within this policy framework, the Joint Research Centre and the European Biodiesel Board have decided to cooperate to investigate the effect of biodiesel on pollutant emissions from diesel engines.
In particular, in this report the effect of biodiesel fuels produced from different raw materials on the regulated emissions from light duty diesel vehicles are compared to the effect on other regulated and unregulated pollutants.

The experimental work described in this report has been performed at the VELA (Vehicle Emission LAboratory) of the Joint Research Centre of the European Commission.

Three different biodiesels were tested:

- Biodiesel 1: a biodiesel consisting of pure rapeseed methyl ester and meeting the specifications of the EN 14214 standard.

- Biodiesel 2: a blend (50% + 50% v/v) of two different biodiesels obtained, respectively, from sunflower oil and from soybean oil
- Biodiesel 3: a biodiesel obtained from palm oil

The biodiesels were tested both neat (with the exception of the one produced from palm oil) and blended with a standard diesel fuel at a percentage of 30%. It was not possible to test the neat biodiesel obtained from palm oil because of its very bad cold properties, being solid at ambient temperature.

The experimental programme consisted in emission tests carried out using two light duty diesel passenger cars according to the current certification legislative procedures. The two vehicles, both complying with the Euro 3 emission standards, mainly differed for the engine technology and in particular for the fuel injection system.

Both the regulated emissions (HC, CO, NOx PM) and emissions not currently regulated (PAH and Volatile Organic Compounds) were measured.

The main findings can be summarized as follows:

In general, it can be said that the use of biodiesel may lead either to a reduction or to an increase of the emissions depending on:

- The pollutant considered
- The diesel fuels used to establish the emission base line
- Content of biodiesel in the fuel
- Vehicle technology and engine settings
- Engine operating conditions
- Driving cycle and driving cycle phase

This study confirms that the influence of biodiesel on pollutant emissions strongly depends on the biodiesel content of the fuel; in general the effects are almost negligible at for low biodiesel and reach a maximum with neat biodiesel. The most substantial effect is observed when neat biodiesel is used; the results obtained suggest that in this case the very different properties of biodiesel compared to a standard diesel fuel make the engine operate in non optimum conditions and, as a consequence, certain pollutants may increase significantly. Furthermore, the results have put in evidence that the cold start is the most critical phase of the cycle; in terms of emissions, the difference between the base diesel fuel and the fuels containing biodiesel are concentrated in the first 200-300 s of the cycle.

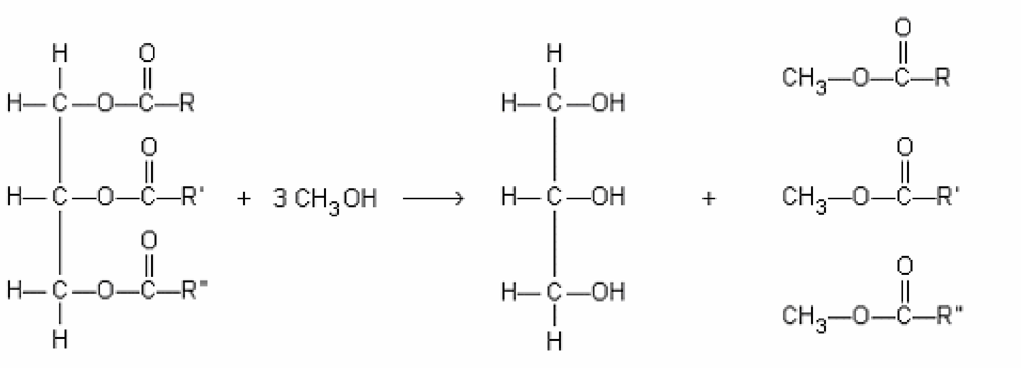
Particulates emissions are in general reduced by biodiesel; in particular soot emissions are reduced to a large extent especially when neat biodiesel is used. However particulate SOF fraction is increased especially at low load, load speeds (urban part of the cycle) and this may results in an increase of the total PM mass compared to the base diesel fuel.

The origin of biodiesel or, in other words, the vegetable oil used to produce the biodiesel, seems to have a very limited effect on emissions. Only in the case of palm oil, its higher cetane number have some positive effects on CO, HC and PAH.

Finally, it has to be pointed out that the study performed by the JRC dealt only with environmental aspects; the impact of the different biodiesel tested on engine performance and on its durability/reliability is not part of the current study.

2 Biodiesel and emissions: introduction

Biodiesel is more correctly defined as Fat Acid Methyl Esters (FAME) and is obtained by reacting vegetable oils of fatty acid (triglycerides) with methanol in the transesterification process:



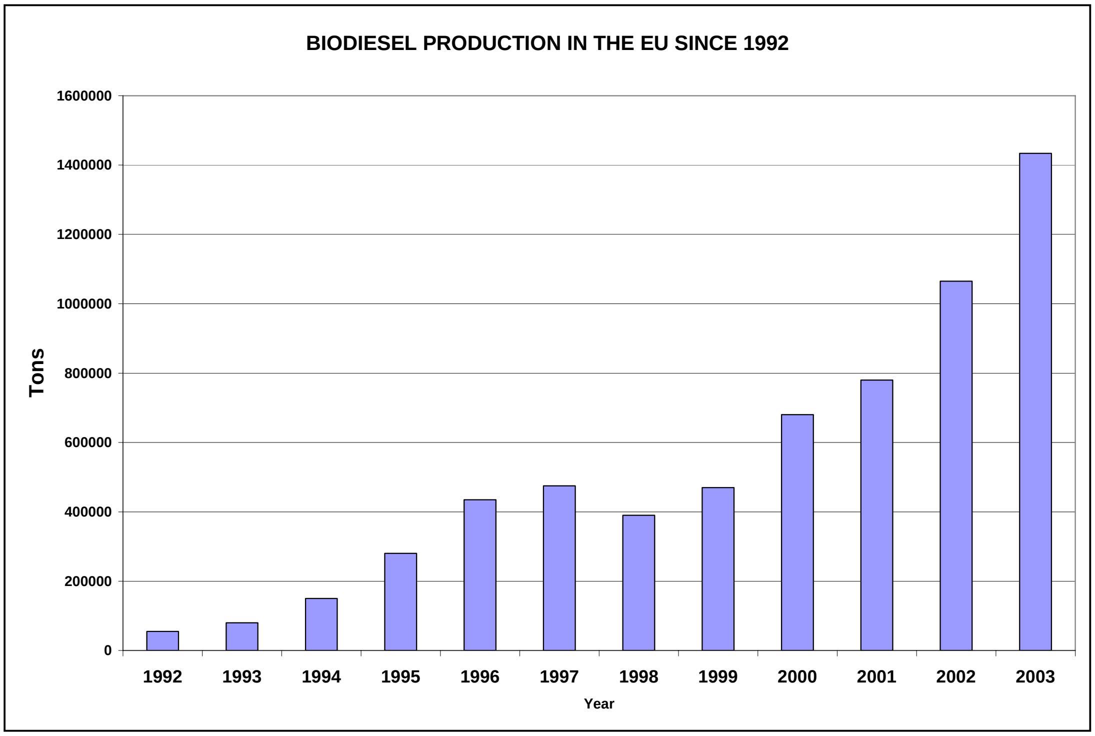
Where R, R' and R" are straight chains with or without double bonds and whose usual number of carbon atoms is 17, though it can be placed between 15 and 23.

The use of methylesters in diesel engines overcomes most of vegetable oils problems, since they present the following properties:

- A much lower viscosity than vegetable oils and close to diesel fuel viscosity; this property implies injection characteristics similar to diesel fuel.
- A lower final boiling point than vegetable oils
- A cetane number close to diesel fuel one or even higher.
- A lower CFPP than vegetable oils; thus allowing the engine use at colder temperatures than vegetable oils.

Biodiesel is currently the most produced biofuel in Europe: the production in 2003 was about of 1500000 (EU25) tons with an increase of more than 32% compared to the 2002 figure.

Fig. 1



Beyond the positive effects on greenhouse gases emissions and on security of energy supply, biodiesel significantly influences pollutant emissions as well. One of the most important characteristics of biodiesel is the presence of oxygen in its molecules; biodiesel contains about 10.8% w/w of oxygen and that affects the combustion process to a large extent.

Effects on emissions of either neat biodiesel or of diesel fuel/biodiesel blends have been investigated in many studies and a lot of data is already available. However, most of these studies have been carried out on heavy duty engines and sometimes they have come to contrasting conclusions.

Regarding gaseous emissions, in general important reductions of HC and CO emissions have been reported with the use of neat biodiesel or diesel/biodiesel blends on heavy duty engines. On the contrary, NOx emissions are generally increased.

Particulate emissions are usually reduced to a large extent but increases have been also reported due to a higher SOF fraction.

The situation is less clear when unregulated emissions are considered, like for example PAHs adsorbed on particulates. Some studies have shown an increase of PAHs emissions while in other cases all emissions resulted to be lowered by the use of biodiesel. Regarding light duty vehicles fewer data are available, however, when biodiesel, either neat or blended with standard diesel fuel, has been tested in these vehicles an increase of particulate emissions has often been observed, while NOx emissions were substantially unchanged. A CO and HC emission decrease was in general noticed.

Also in the case of unregulated emissions most of the data available have been obtained from tests on heavy duty engines; as already mentioned, contrasting results have been obtained: both decreases and increases in PAH emissions have been reported. The situation is very similar for other unregulated pollutants as aldheydes and ketones and therefore there is no a clear picture about the effect of biodiesel on these emissions.

There are several factors that can explain why sometimes experimental works have led to conflicting conclusions on the effects of biodiesel on emissions from diesel vehicles:

- The behaviour of a fuel strongly depends on the engine/vehicle in which it is tested; in particular emission tests may give very different results if carried out on light duty vehicles rather than on heavy duty engines (and *vice versa*). This is mainly due, in addition to the different engine/aftertreatment technology, to the differences in the tests itself and more specifically in the test cycle (cold start/hot start, transient/stationary,…).
- Biodiesel can be tested either neat or blended with diesel fuel in different percentages. Of course the effect on emissions depends on the content of biodiesel in the fuel.
- The diesel fuel used as term of comparison; the evaluation of the emission performance of a biodiesel depends on the quality of the base fuel as the properties of the diesel fuel determine the emission "baseline". The difference in emissions between two very different diesel fuels, especially with older vehicle technologies, can be very remarkable and are often of the same order of magnitude of the variation noticed when testing biodiesel.
- As well known the test cycle has a huge influence on emissions and consequently also the emission performance assessment of different fuels depends on the specific test performed.
- The effect of biodiesel on emissions of light duty vehicles is significantly different from the effect on emissions of heavy duty engines. The main reason, beyond the differences in engine technology, is the very different test procedure used to measure pollutant emissions. For example, the HD emission test is always carried with a warmed up engine while the emission test for LD vehicles includes a cold start that represents the main contribution to the whole emission measured over the test cycle.

The emissions of a diesel engine are influenced to a significant extent by fuel quality. Some fuel properties have a stronger influence than others and, comparing a standard diesel fuel with a typical biodiesel, these properties may be very different (see table 1):

Table 1

		Typical values	
		Gasolio	Biodiesel (RME)
Density @15 °C	kg/m3	820-845	860-900
Sulphur Content	mg/kg	0-50	0
Cetane Number		51-55	51-55 or higher
Polycyclic Aromatic Hydrocarbons	% wt/wt	0-11	0
Distillation Range	°C	180-360	320-370
Oxygen content		0	~10.8
Lower heating value	MJ/kg	42	37-38

Table 1 shows clearly that, besides the chemical composition, a standard diesel fuel differs from a biodiesel for a number of properties. That has a direct impact on the injection and the combustion of the fuel:

- The higher density of the biodiesiel means that injecting the same volume of fuel the mass of biodiesel injected is higher.
- To obtain the same power output from the engine, about 10-11% more biodiesel have to be injected in the engine to compensate the lower heating value. As a consequence, at the same operating conditions (torque and rpm) the duration of the injection will be longer.
- The higher average boiling point of the biodiesel has an obvious influence on the air/fuel mixing process as it will take more time to vaporize the fuel injected.

From a theoretical point of view, as soon as fuel injection into the cylinder commences, a distribution in the Air/Fuel ratio across the fuel spray develops (see fig. 2). The most external area is characterized by a very high A/F ratio due to the over-mixing of fuel with air; this part of fuel has mixed with air beyond the lean limit of combustion and will not auto-ignite. The amount of fuel that over-mixes with air increases rapidly with time. On the contrary, in the most internal area of the spray the A/F is very low and there is not enough oxygen for a complete combustion.

When the charge ignites, all the fuel mixed with air within the air/fuel ratio limits of combustion will burn very quickly (premixed combustion phase) while the rest of the fuel will burn as soon as it reaches the right A/F value (mixing-controlled combustion phase) (see fig. 3). The part of fuel over-mixed with air that cannot burn will contribute to the unburned hydrocarbons while the part of fuel not sufficiently mixed with air will contribute to the soot formation.

The process above described is affected by biodiesel in several ways to an extent that depends on the biodiesel content: first of all, the inner part of the spray will have a more favourable A/F ratio due to the oxygen present in the biodesel molecules. Moreover, the larger amount of fuel injected and the higher boiling point of biodiesel will significantly affect the air/fuel mixing process with effects on emissions not easy to predict.

Another parameter that may change significantly with biodiesel is the injection duration: to inject a larger volume of fuel (to compensate for the lower heating value), the duration of injection will be longer. One of the main sources of unburned hydrocarbon is the fuel that leaves the injector nozzle at low velocity late in the combustion process. The longer fuel injection can increase the amount of fuel injected in the combustion process during the latest phases of the combustion process and that could lead to an increase of hydrocarbon emissions.

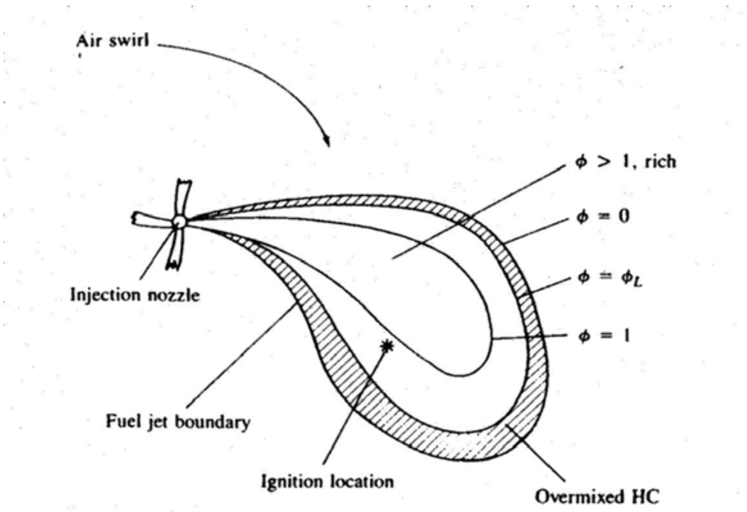


Fig. 2 – Air/fuel ratio distribution after diesel injection in the combustion chamber

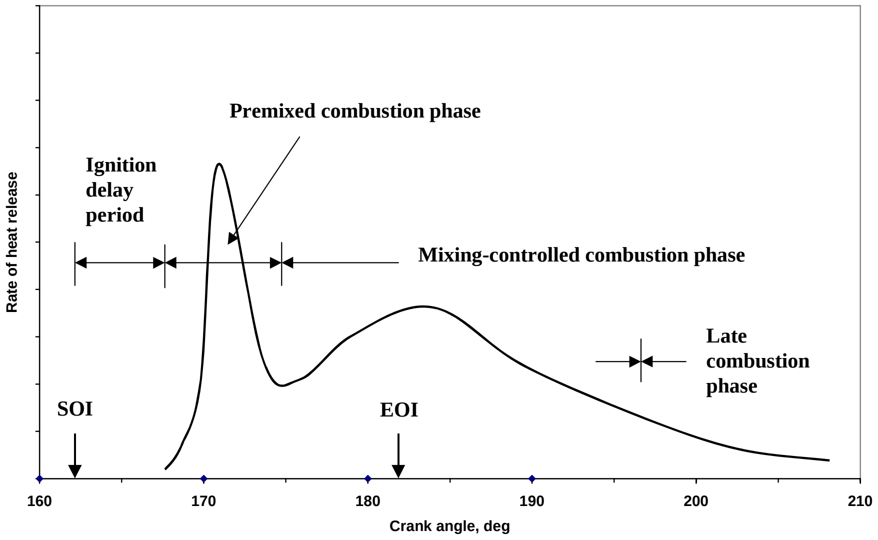


Fig. 3 – Typical combustion process of a compression ignition engine.

3 Experimental work

3.1 Test Fleet

The test fleet consisted of two diesel passenger cars mainly differing for model and engine technology. In particular one vehicle featured the "common rail" injection system while the other one the "unit injector" technology. Both the vehicles were not equipped with a particulate trap.
The main data of the vehicles are listed here below (table 2):

Table 2

Vehicle Type	Passenger car	
	Vehicle 1	**Vehicle 2**
Emission level	EURO 3	EURO 3
Category	M1	M1
Displacement (cm3)	1910	1896
Max. Power (kW @ rpm)	85 @ 4000	96 @ 4000
Inertia Class (kg)	1265	1470
Cylinder	4	4
Max. Torque (Nm @ rpm)	255 @ 2000	285 @ 1750
Aspiration	Turbocharged	Turbocharged
Combustion Type	DI	DI
Injection System	Common Rail	Unit Injector
EGR Y (yes) N (no)	Y	Y
Oxidation Catalyst Y(yes) N(no)	Y	Y
Year	2004	2004
Odometer reading	1325	3122

3.2 Test fuels

One of the main objectives of this study was to investigate the effect on emissions of biodiesel produced from different raw materials. In particular, three different biodiesel were considered:

1. Biodiesel consisting of pure rapeseed methyl ester and complying with the EN 142214 specifications (hereinafter **Biodiesel 1**)
2. Blend of two different biodiesels respectively obtained from soybean and sunflower oil (50% Soybean Methyl Esters + 50% Sunflower Methyl Esters) (hereinafter **Biodiesel 2**)
3. Biodiesel produced from palm oil (hereinafter **Biodiesel 3**)

These biodiesels were tested both neat (with the exception of the one produced from palm) and blended with a standard diesel fuel at a percentage of 30%. As a consequence, the final test matrix comprised six different fuels:

The original test fuel matrix comprised 6 different test fuels described here below:

1. EN 590 standard diesel fuel (Fuel 1, Tab. 6)
2. Fuel 1+ 30 % Biodiesel 1
3. Neat Biodiesel 1
4. Neat Biodiesel 2
5. Fuel 1 + 30% Biodiesel 2
6. Fuel 1 + 30% Biodiesel 3

It was not possible to test the neat Biodiesel 3 because of its cold properties (its CFPP is about 10 °C).

After the emission tests originally planned had been completed, it was decided to integrate the emission data testing, only on the Vehicle 2, a second commercial diesel fuel (Fuel 2, table 3) and the 30% blends with the three biodiesels. These further tests were performed to investigate the effect of the reference fuel quality.

Table 3 – Base fuels properties

Property	**Unit**	**Fuel 1**	**Fuel 2**
Density @ 15 C	kg/l	0.824	0.839
Sulphur Content	mg/kg	<10	45
CFPP	° C	- 15	- 16
Cetane Number		53.5	51.5
Distillation			
10 % vol	° C	199	223
50 % vol	° C	269	274
90 % vol	° C	339	343
95 % vol	° C	357	358
Total Aromatics	% v/v	20.2	29.8
Polyaromatics	% v/v	3.5	5.0

Table 4 – Biodiesel properties

Property	**Unit**	**Biodiesel 1**	**Biodiesel 2**	**Biodiesel 3**
Density @ 15 C	kg/m3	884.4	884.9	876.1
Cetane Number		61	56.6	65.2
Distillation				
10 % vol	° C	348	347	336
50 % vol	° C	351	350	341
90 % vol	° C	353	352	351
95 % vol	° C	355	355	353
Iodine Number	$gI_2/100g$	111.7	125.3	53
Ester Content	% w/w	96.88	98.20	97.6
Water	mg/kg	538	510	250
Monoglyceride	% w/w	0.58	0.32	0.57
Diglyceride	% w/w	0.14	0	0.12
Triglyceride	% w/w	0.03	0	0.01
Total Acidity	mg KOH/g	0.40	0.45	0.23
Glycerin	%	0.01	traces	0.01
Methyl Linoleate	% w/w	5.6	0.75	0.54

3.3 Emission tests

The emission tests were carried out on a chassis dynamometer using the New European Driving Cycle (NEDC). Regulated emissions (HC, CO, NOx and Particulates) were measured following the legislative measuring procedures. At least two back-to-back tests were carried out with each test fuel on each vehicle. For each fuel, the results of the two back-to-back tests were compared in order to evaluate their repeatability and to ensure that they fell within the expected test error range.
The acceptance criteria used are the same as the ones defined in the EPEFE programme and are reported in the table 5. The acceptability of repeatability of the tests on each fuel was judged on the following basis:

- Ratio: (Max. result)/ (Min. result) < factor (Where factors are in table 5).

If the results of the two back-to-back tests did not match the acceptance criteria, a third test was performed.

Table 5: repeatability criteria

Back to back acceptance criteria							
LD diesel	HC <0.05g/km	HC >0.05g/km	CO <0.10g/km	CO >0.10g/km	NOx	Pm <0.06g/km	Pm >0.06g/km
Factor: Max/Min	1.65	1.40	1.55	1.35	1.15	1.40	1.25

3.4 Instrumentation details

Regulated pollutant emissions were measured using a chassis dynamometer and a conventional CVS system with a critical flow Venturi.

To follow the legislative cycle, the driver was assisted by a driver aid system.

Emission measurements were performed using the following analysers:

- **CO**: IR analyser.
- **NOx**: Chemiluminescence analyser.
- **HC**: FID analyser.
- **Particulate mass**: particulate samples were collected according to the legislative procedure for diesel vehicles using Pallflex T60A20 filters and the mass was determined by weighing.

A schematic layout of the emission test facility is illustrated in figure 4.

Mass/size distribution

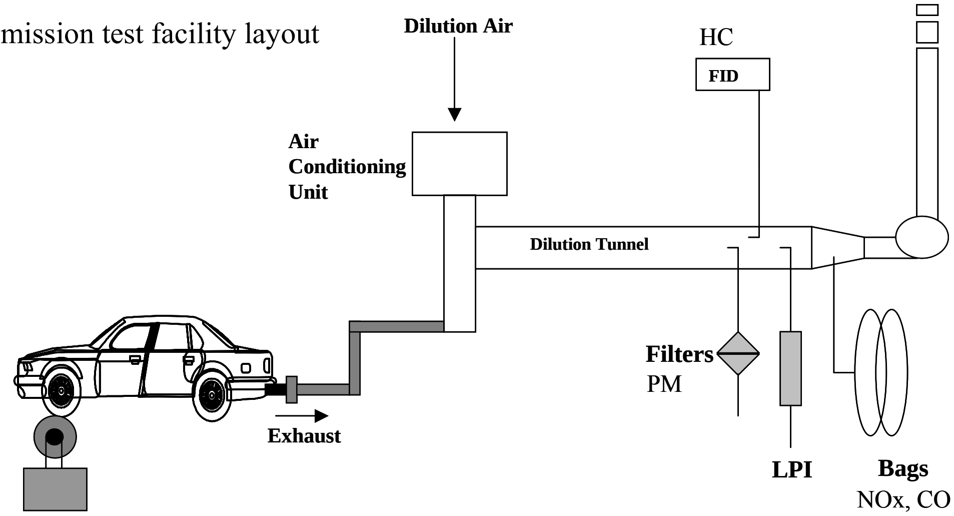
In addition to the total mass measurement as required by the legislation, particulate emissions were characterized in terms of mass/size distribution using a 12 stages Low Pressure Impactor.

The LPI used in this experimental programme has the following main features:

- Manufacturer: Hauke GmbH
- 12 stages
- Volume flow rate: 25 l/min
- Measuring range: 0.0085 µm-16 µm (aerodynamic diameter)

Before starting the measurements, the LPI is disassembled and a previously weighed aluminium foil with a suitable shape is placed on the plate of each stage. Once the LPI has been assembled again, it is connected to an isokinetic sampling probe located on the dilution tunnel and to a suction pump. After the test, each aluminium foil is weighed again to measure the mass of the particulates collected on it.
To avoid condensation of water vapour the impactor was heated up at 50 °C with a heating jacket.

Fig. 4 – Typical emission test facility layout



4 Results

4.1 Regulated Emissions

4.1.1 Gaseous Emissions – Base Fuel 1

The results of the tests carried out on both the test vehicles are plotted in the figures 5-20. The measured emission levels are reported for the whole driving cycle (combined) and for both the urban (ECE15) and extra-urban (EUDC) phases. The percentage variations of the emissions in comparison with those obtained with the base fuel are reported in the tables 6-7.

The use of biodiesel, neat or blended with the standard diesel fuel, resulted in an increase of unburned hydrocarbon (HC) and CO emission levels in both the test vehicles. This increase was much more evident in the urban part of the cycle and specifically just after the cold start: in particular the HC emission increase is concentrated approximately in the first 100 seconds of the cycle. This difference almost disappeared after the first sub-cycle of the urban part. Over the extra-urban part of the cycle CO and HC emission levels were in general very low and the differences among the test fuels negligible.

In the case of the Vehicle 1 the increase of HC e CO emissions was larger with the neat biodiesel than for the 30% blends; for Vehicle 2 it is more difficult to draw reliable conclusions concerning the comparison between neat biodiesel and the 30% blends as some of the measurements are affected by a higher variability.

In general the three different types of biodiesel tested had very similar effects on emissions; only in the case of CO and HC a certain influence of the biodiesel quality was noticed. The blend containing biodiesel from palm oil (Biodiesel 3), gave the lowest HC and CO emissions compared to the fuels containing biodiesels obtained from other vegetable oils. This result is probably due to the composition of the biodiesel from palm oil that, in general, corresponds to a higher cetane number thanks to its higher content of linear hydrocarbons.

CO emissions were above EURO 3 limit when the neat biodiesel fuels were tested in vehicle 1 (Figure 9). This situation did not happen in the tests performed on vehicle 2 (Figure 11).

NOx emissions were affected to a lesser extent by the fuels containing biodiesel; only with the neat biodiesel gave NOx emissions somewhat higher than the standard diesel.

The NOx levels measured over the urban and the extra-urban parts of the cycle suggest also that the two test vehicles had different engine settings; in fact, while the Vehicle 1 exhibited the highest NOx values over the urban part of the cycle, the Vehicle 2 showed an opposite behaviour. This could be the consequence of a different emission control/performance strategy and could also explain, at least partially, the different effects of biodiesel on the emissions of these two cars.

Table 6 : Vehicle 1 - Percentage variations of emissions (mean values) compared to Base Fuel 1

VEHICLE 1	Base Fuel 1 + 30%Bio 1	Base Fuel 1 + 30%Bio 2	Neat Bio 1	Neat bio 2	Base Fuel 1 + 30%Bio 3
Combined					
HC	29%	37%	237%	271%	16%
CO	30%	36%	186%	200%	3%
NOx	1%	-3%	4%	16%	-2%
PM	-23%	-32%	-66%	-70%	-27%
ECE 15					
HC	33%	41%	259%	294%	16%
CO	30%	36%	183%	196%	3%
NOx	1%	-3%	-5%	4%	-3%
PM	4%	-31%	-31%	-37%	-24%
EUDC					
HC	13%	25%	144%	181%	25%
CO	71%	71%	786%	843%	5%
NOx	0%	-4%	14%	41%	-1%
PM	-28%	-32%	-74%	-77%	-29%

Table 7: Vehicle 2 - Percentage variations of emissions (mean values) compared to Base Fuel 1

VEHICLE 2	Base Fuel 1 + 30%Bio 1	Base Fuel 1 + 30%Bio 2	Neat Bio 1	Neat bio 2	Base Fuel 1 + 30%Bio 3
Combined					
HC	21%	53%	32%	45%	6%
CO	36%	56%	107%	126%	22%
NOx	6%	2%	16%	19%	0%
PM	1%	-8%	-2%	-3%	-10%
ECE 15					
HC	27%	65%	55%	70%	11%
CO	36%	60%	112%	133%	22%
NOx	5%	1%	10%	13%	1%
PM	8%	0%	40%	38%	-6%
EUDC					
HC	-5%	6%	-54%	-52%	-12%
CO	37%	7%	18%	11%	12%
NOx	7%	3%	19%	22%	4%
PM	-10%	-18%	-45%	-46%	-17%

Fig. 5 –Vehicle 1: Hydrocarbon Emissions - combined

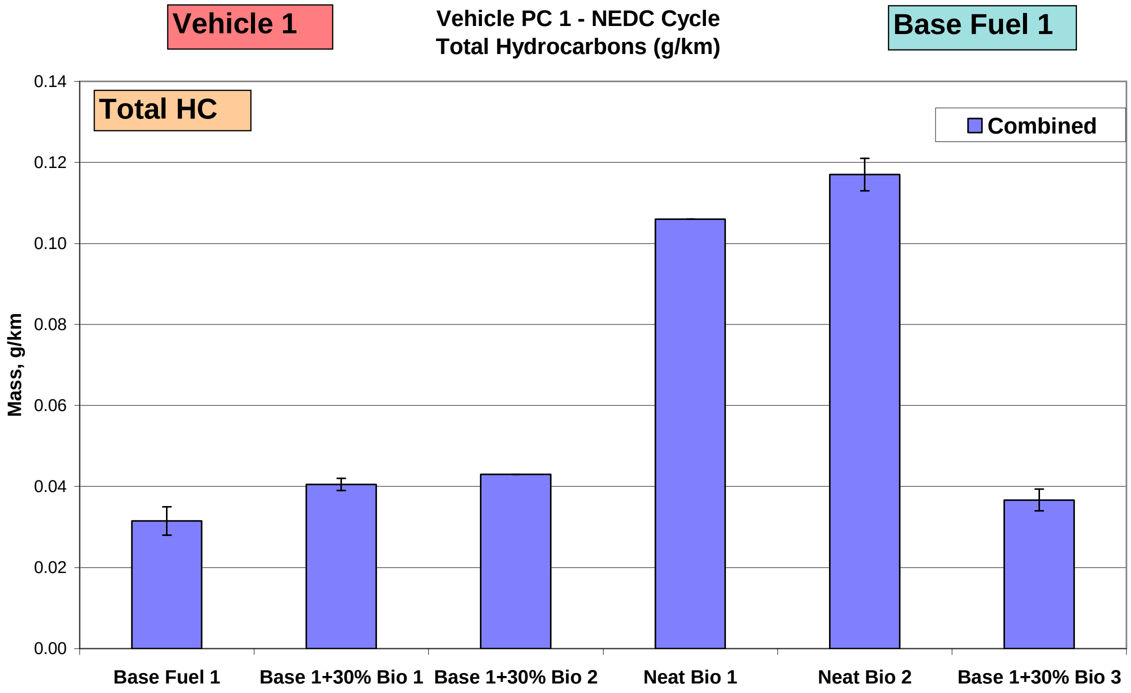


Fig. 6 –Vehicle 1: Hydrocarbon Emissions

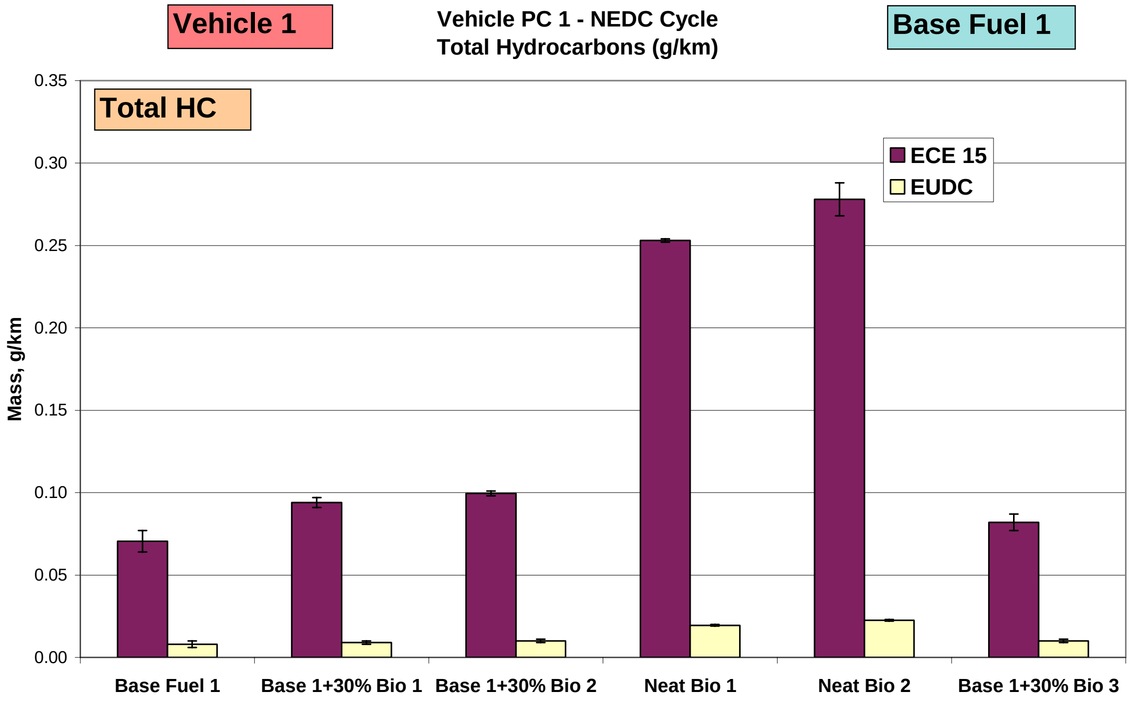


Fig. 7 –Vehicle 2: Hydrocarbon Emissions - combined

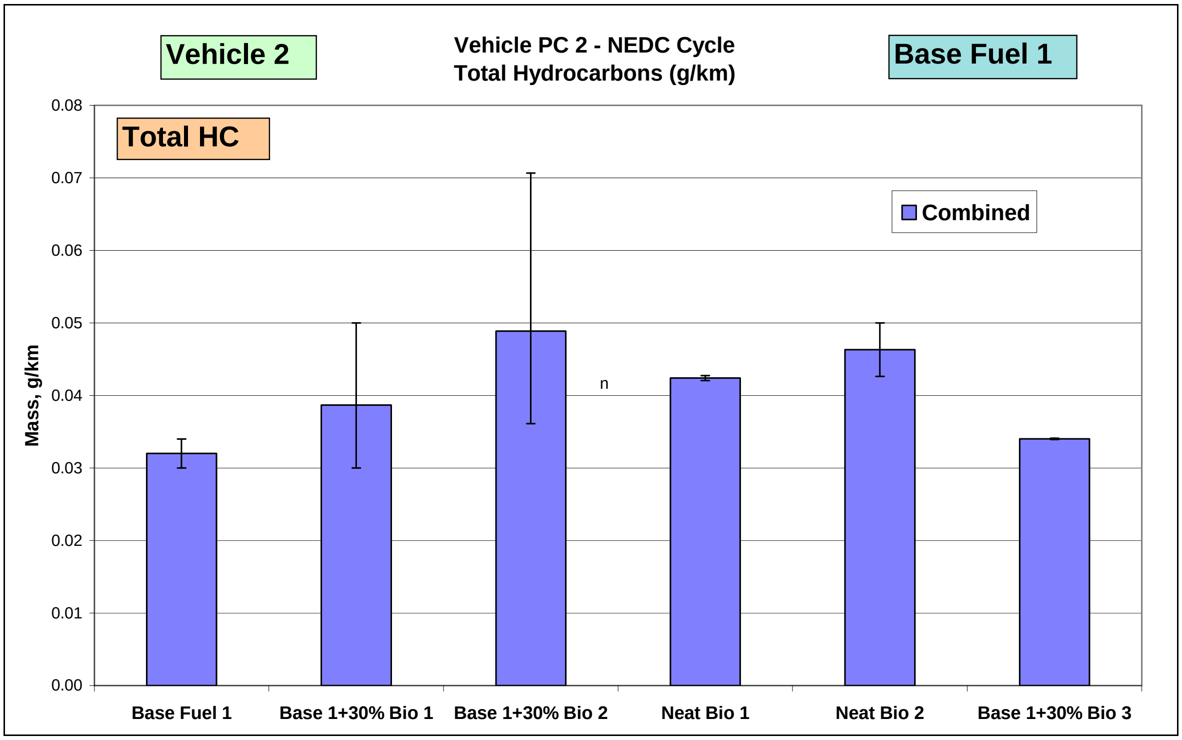


Fig. 8 –Vehicle 2: Hydrocarbon Emissions

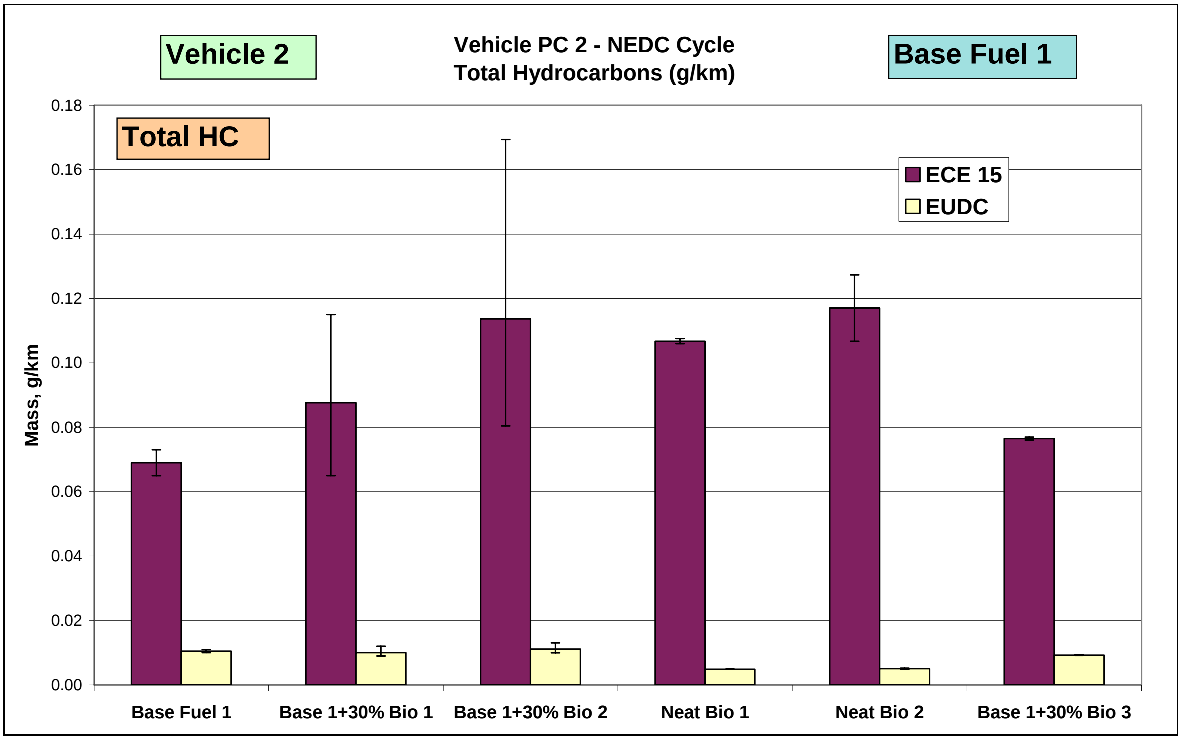


Fig. 9 –Vehicle 1: CO Emissions – combined

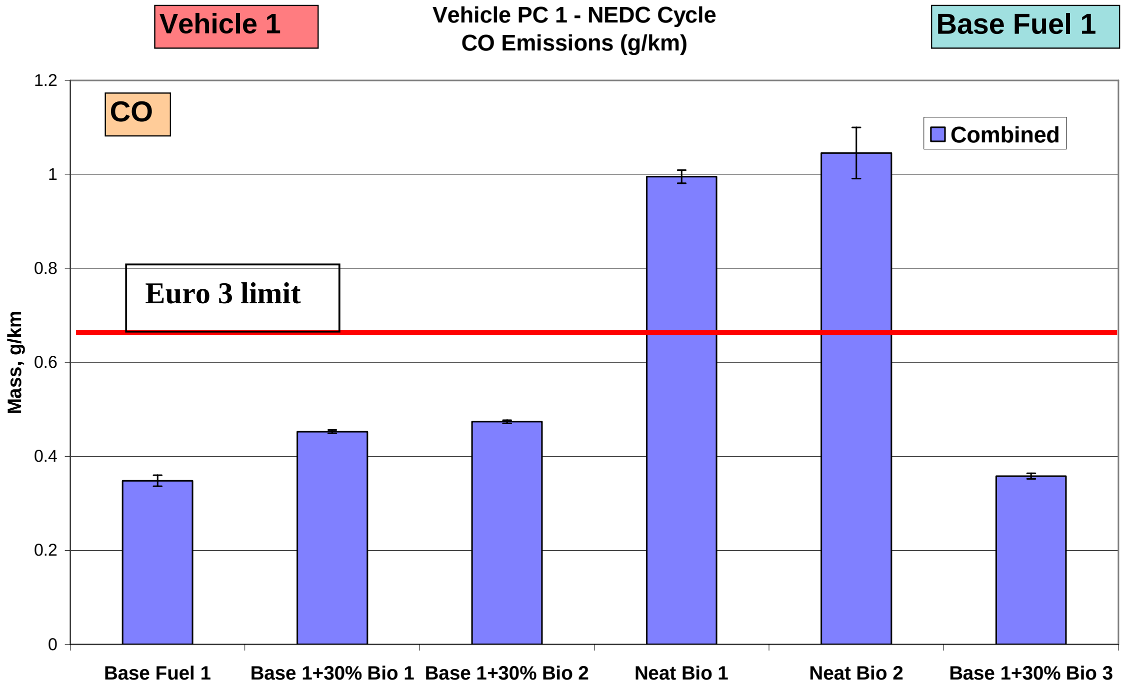


Fig. 10 –Vehicle 1: CO Emissions

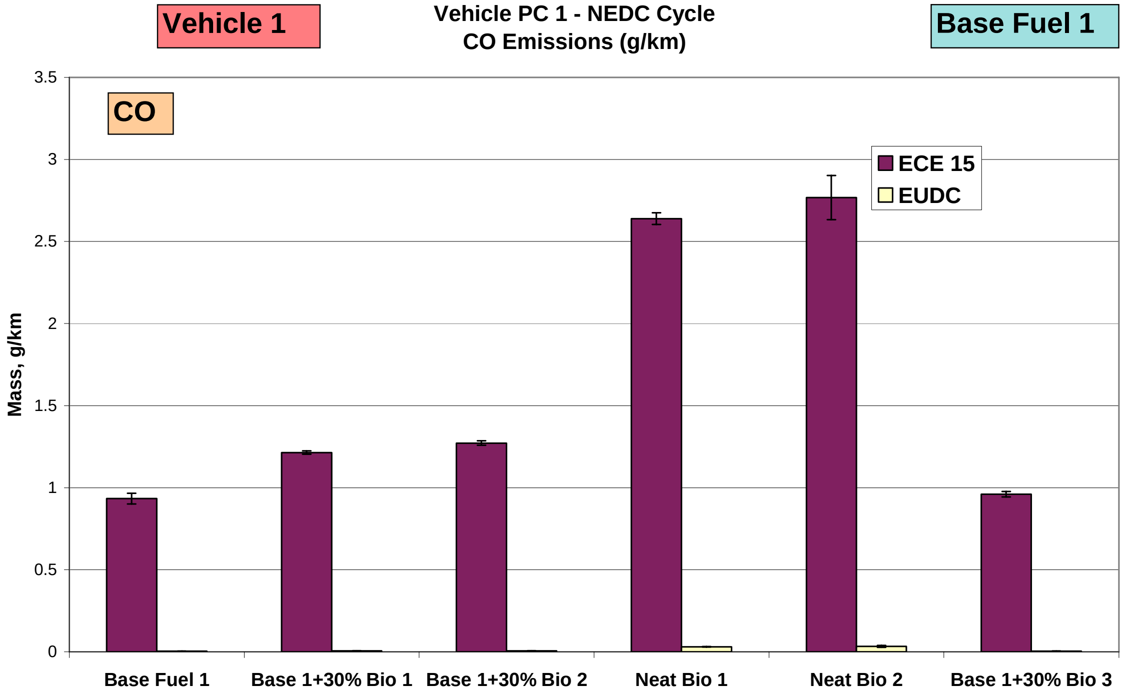


Fig. 11–Vehicle 2: CO Emissions – combined

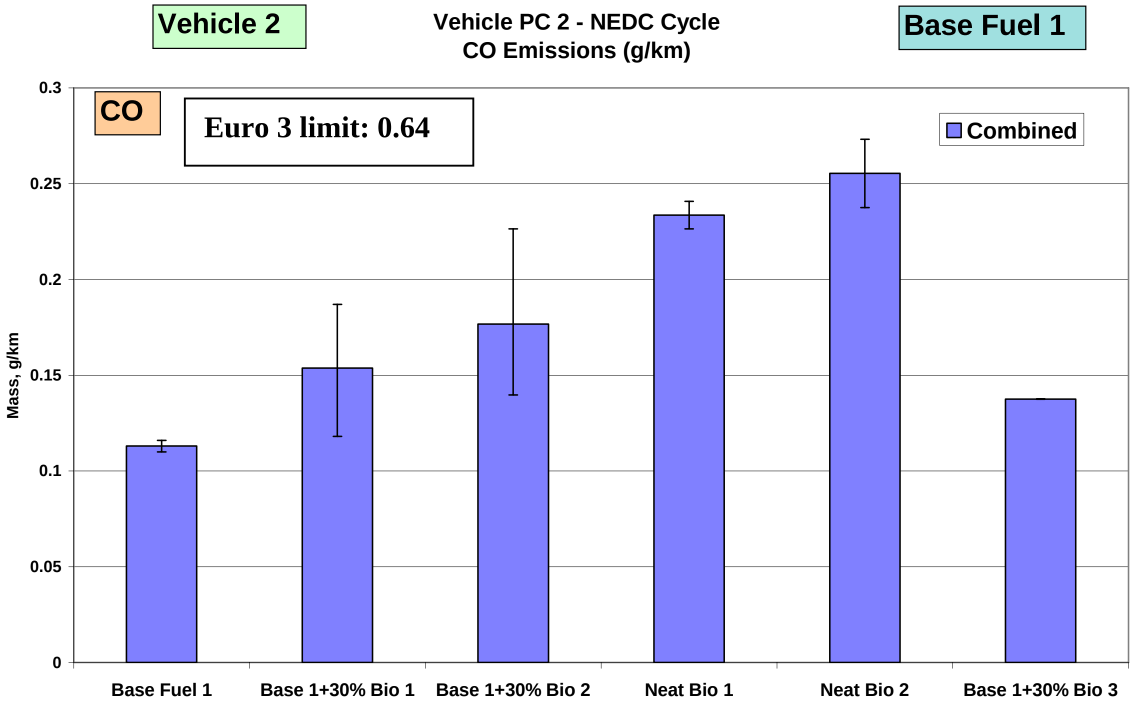


Fig. 12 –Vehicle 2: CO Emissions

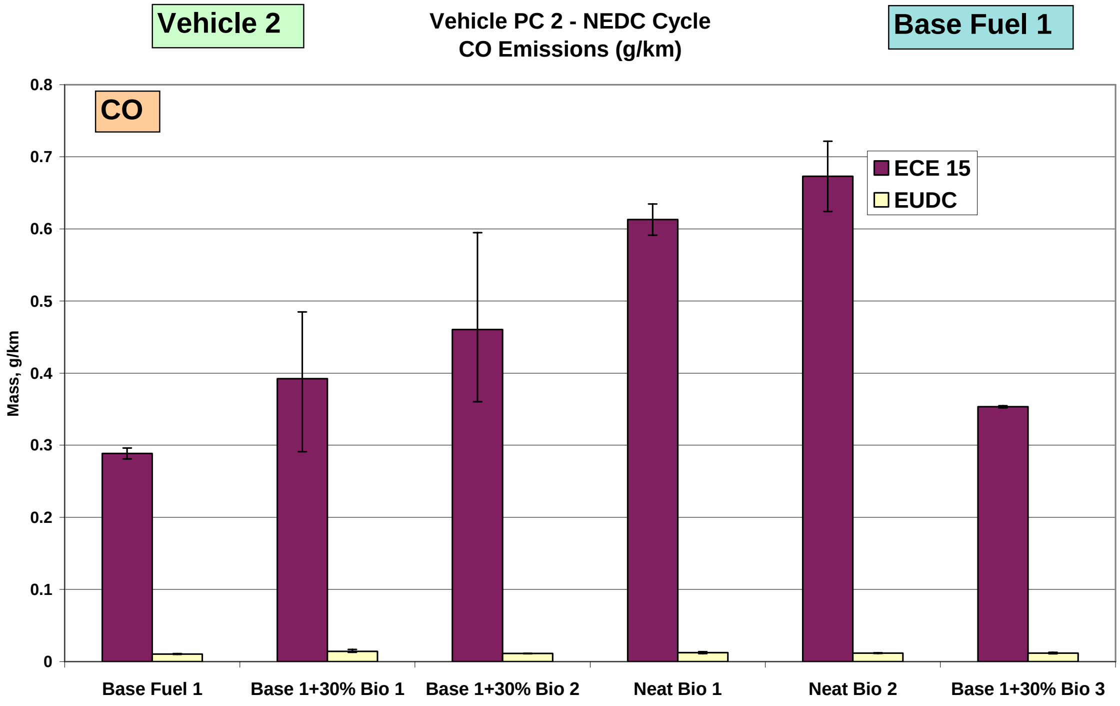


Fig. 13 –Vehicle 1: NOx Emissions - combined

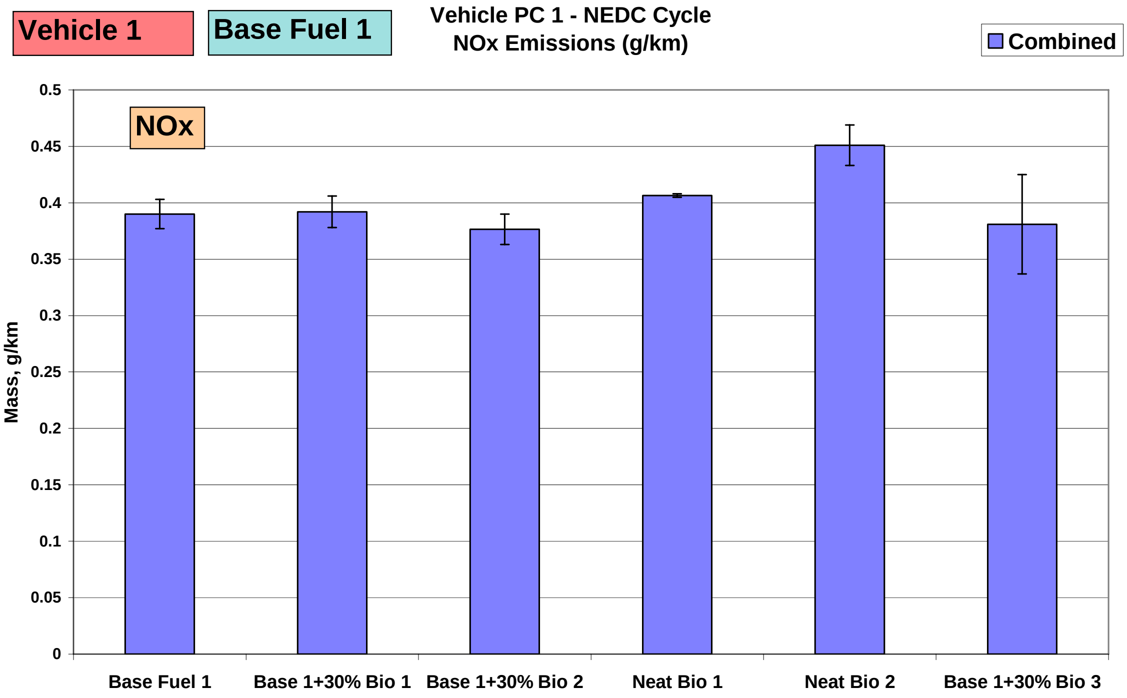


Fig. 14 –Vehicle 1: NOx Emissions

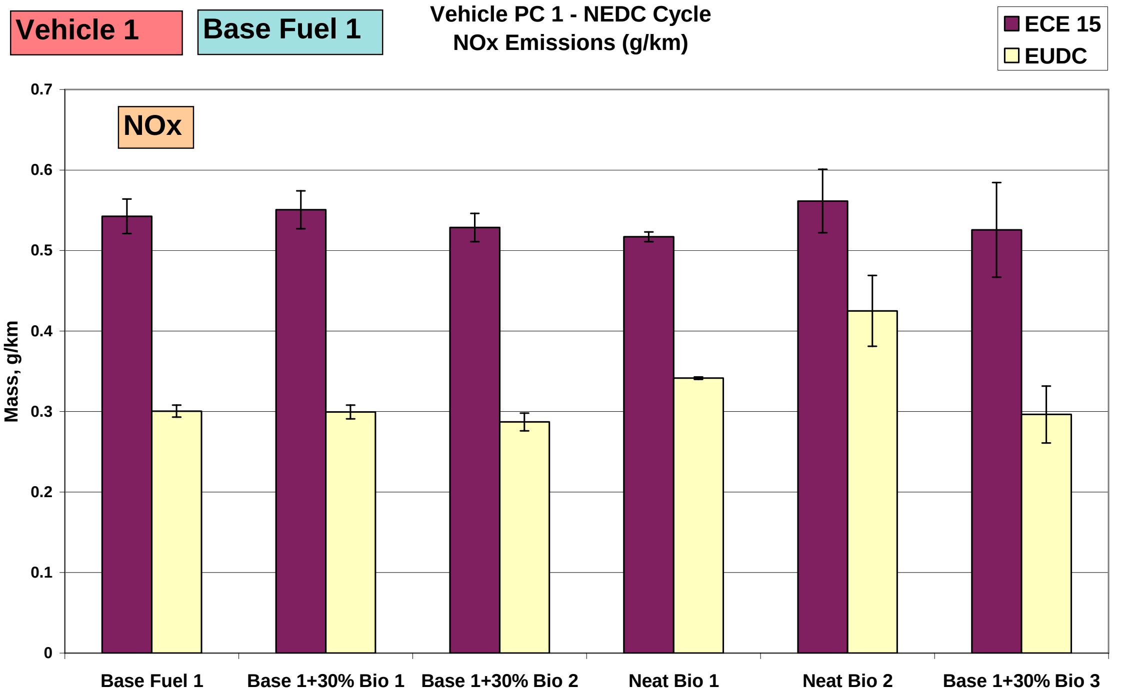


Fig. 15 –Vehicle 2: NOx Emissions - combined

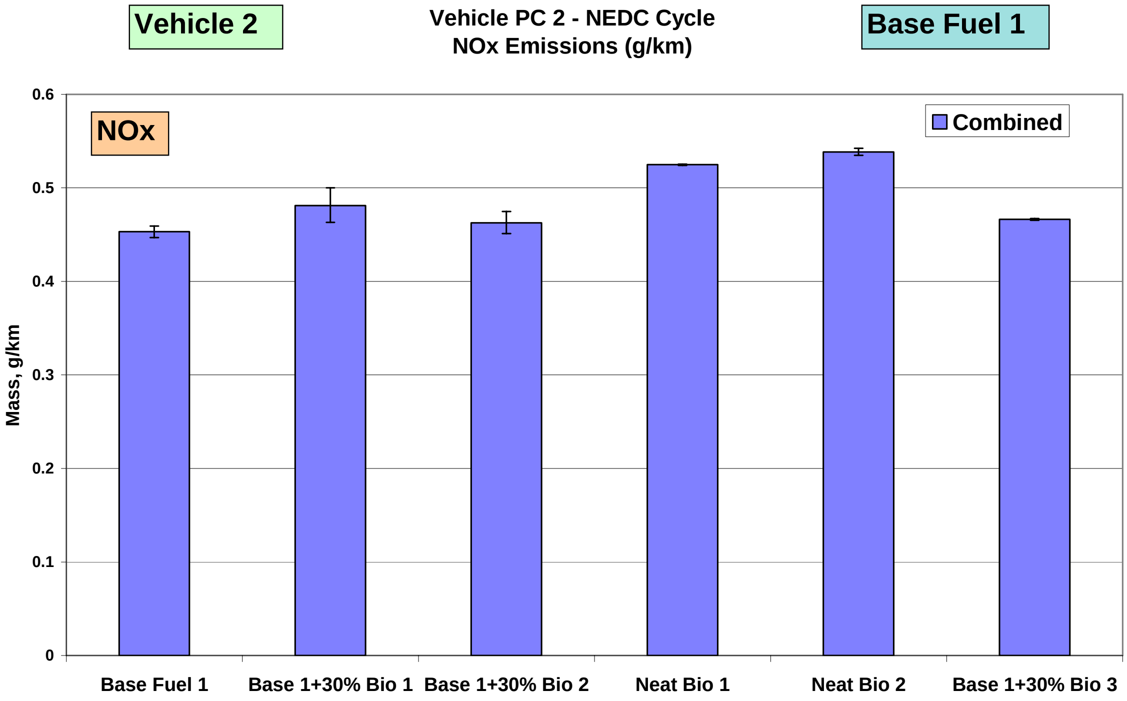


Fig. 16 –Vehicle 2: NOx Emissions

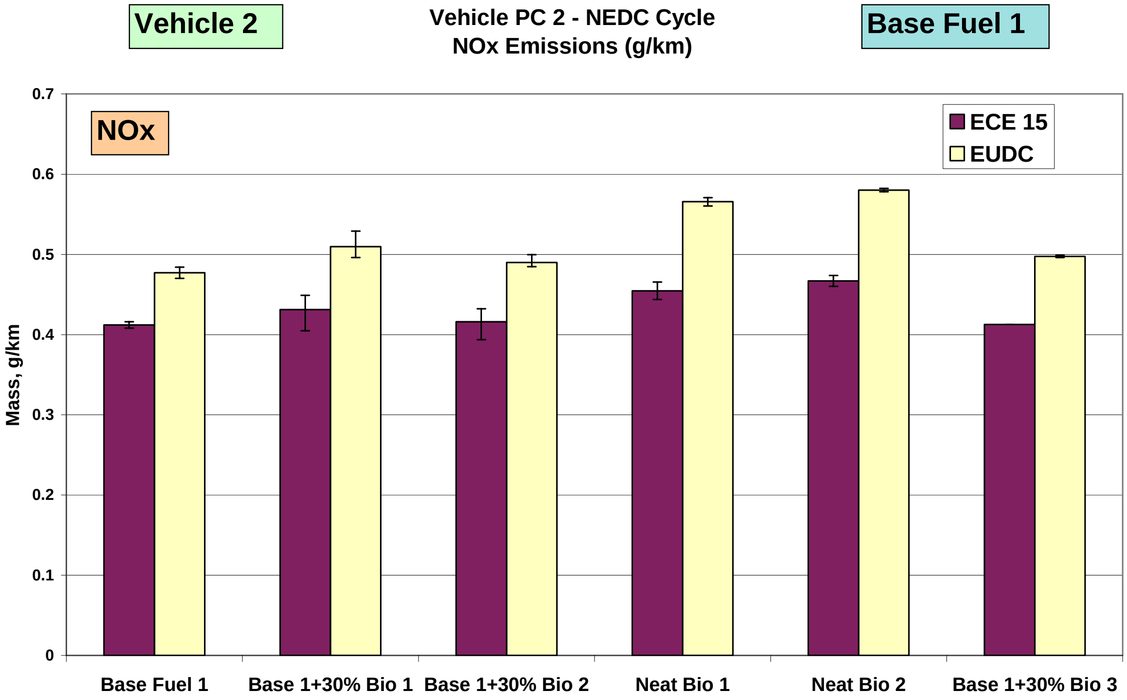


Fig. 17 –Vehicle 1: HC+NOx Emissions - combined

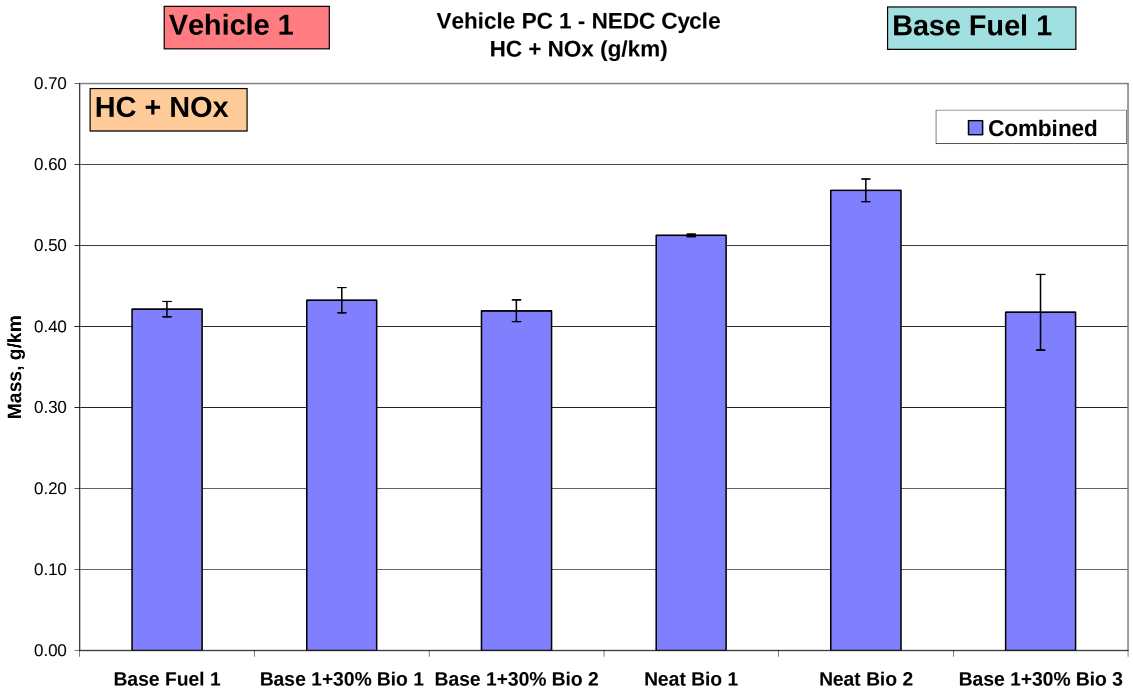


Fig. 18 –Vehicle 1: HC+NOx Emissions

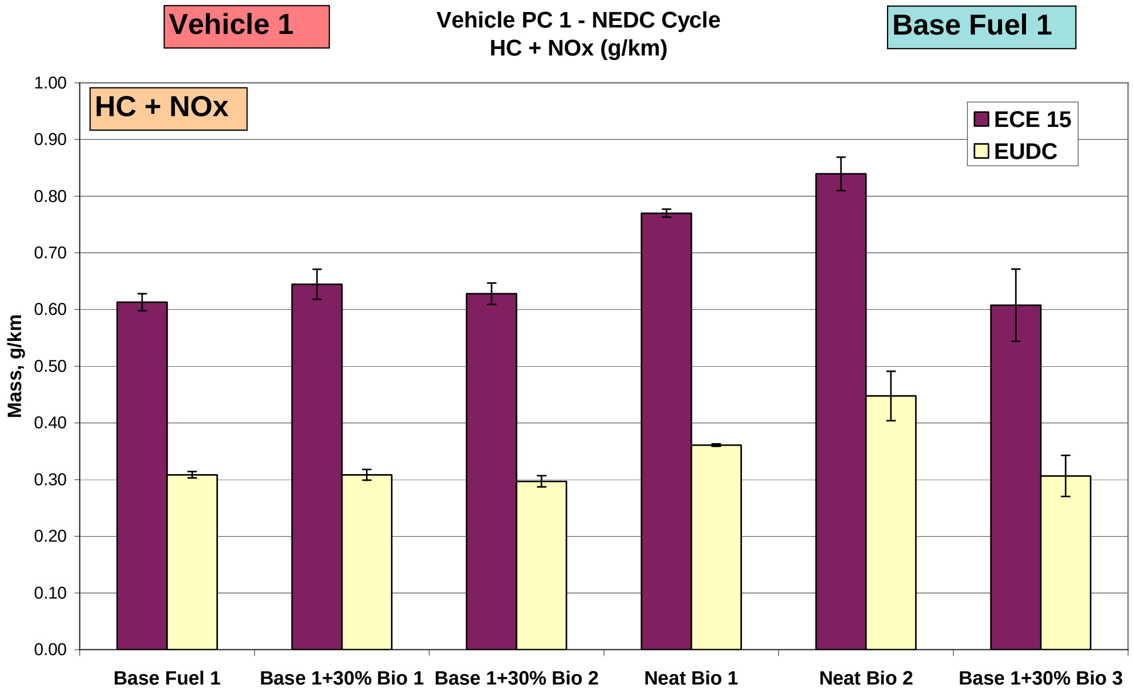


Fig. 19 –Vehicle 2: HC+NOx Emissions - combined

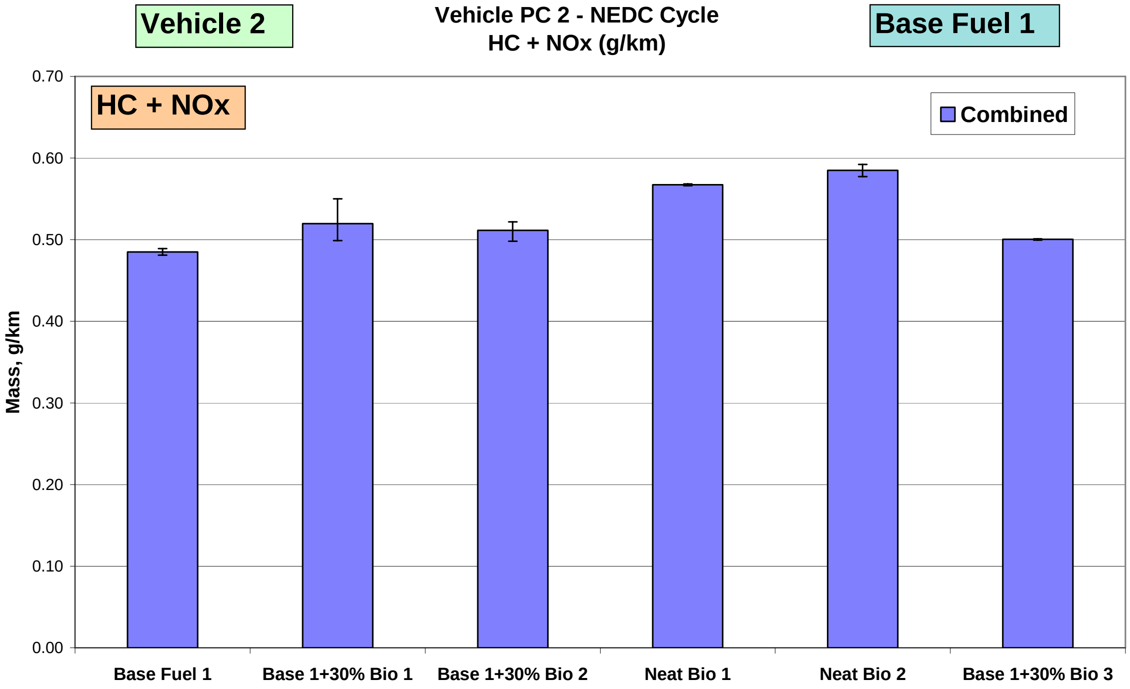
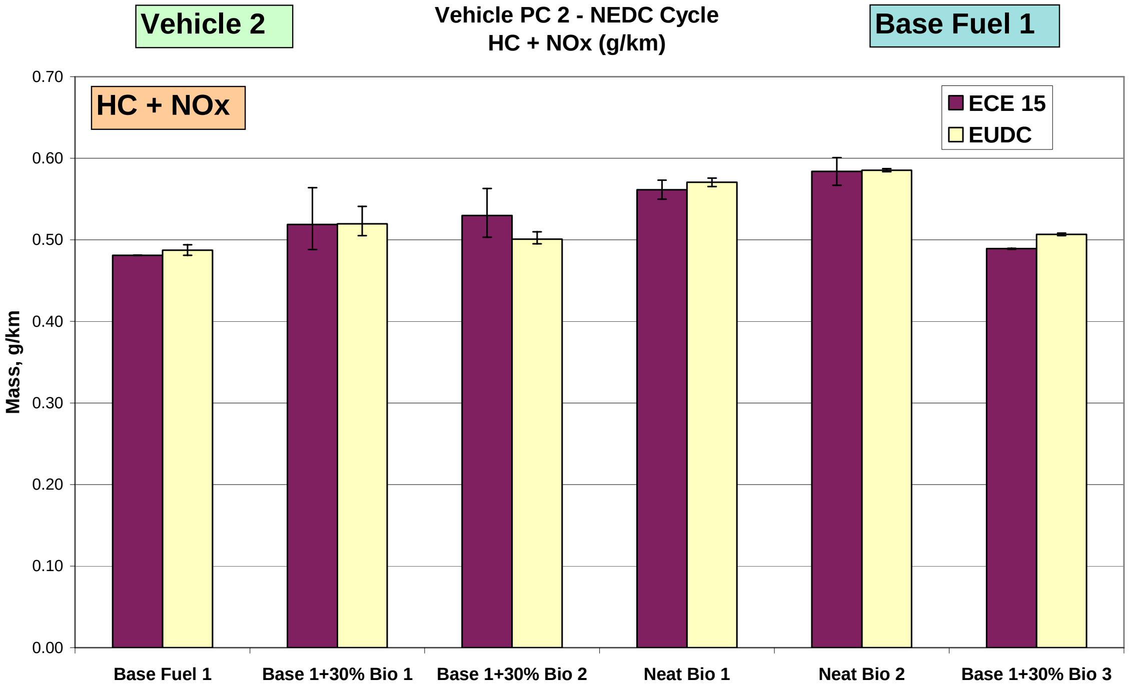


Fig. 20 –Vehicle 2: HC+NOx Emissions



4.1.2 Particulate emissions – Base Fuel 1

As far as particulate emissions are concerned (fig. 21 and 22), the effect of the fuels containing biodiesel turned out to be very different for the two cars.

In the case of Vehicle 1 a reduction of particulate emissions was noticed with all the fuels containing biodiesel; the PM mass reduction ranged from -23% to -32% with the 30% blends while the two neat biodiesel fuels had the largest effect with a reduction of the combined total mass of -66% (Bio 1) and -70% (Bio 2). Furthermore, particulate emissions were reduced both over the urban and the extra-urban part of the cycle, even if the effect was in general larger over the extra-urban phase. For this vehicle, only base fuel 1 was used as reference fuel.

Particulate emissions of the Vehicle 2 were affected by fuels containing biodiesel in a completely different way: while over the extra-urban part of the cycle part the two neat biodiesels led to an important reduction of the total mass (-45% and –46% respectively with Bio 1 and Bio 2), the emission levels increased by 40% (Bio 1) and 38% (Bio 2) over the urban phase. The reduction of particulate emissions over the EUDC phase and the increase over the ECE 15 were very similar in magnitude; as a result, the combined value showed no difference compared to the emissions obtained with the standard diesel fuel.
Moreover, the 30% blends had a very little impact on particulate emissions especially over the urban part of the cycle; the EUDC particulate emissions were instead slightly reduced (from –10% to –18%).

The different distribution of particulate emissions over the test cycle seems to confirm that the engine settings (EGR ratio, injection advance, etc.) of the two cars were quite different, as already mentioned above (see the section on gaseous emissions); Vehicle 1 had in fact higher particulate emissions over the EUDC than the ECE15 cycle, while Vehicle 2 exhibited an opposite behaviour. Moreover, also the absolute levels of particulate emissions were different: close to the Euro 3 limit in the case of Vehicle 1 and below the Euro 4 limit (even if the vehicle was certified for the Euro 3 emission standards) for Vehicle 2. These differences could contribute to explain the diverse response to the fuel exhibited by the two vehicles.

Biodiesel quality did not appear to play an important role on particulate emissions: the effects are in fact very similar for all the three different biodiesels tested.

Fig. 21 –Vehicle 1: PM Emissions - combined

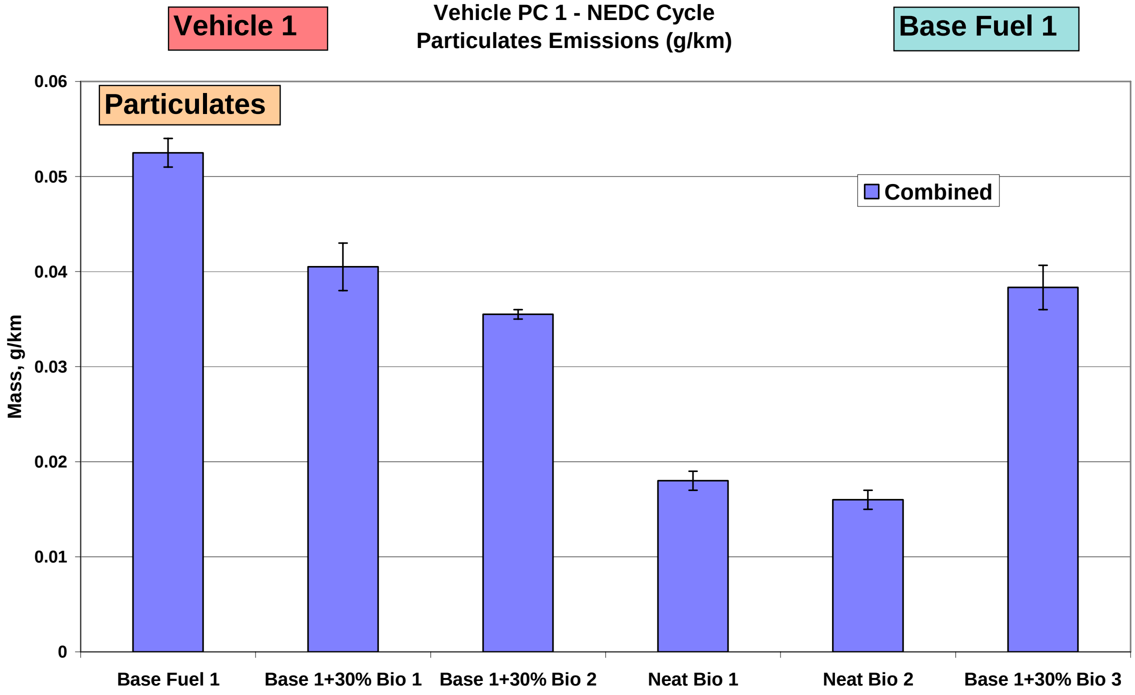


Fig. 22 –Vehicle 1: PM Emissions

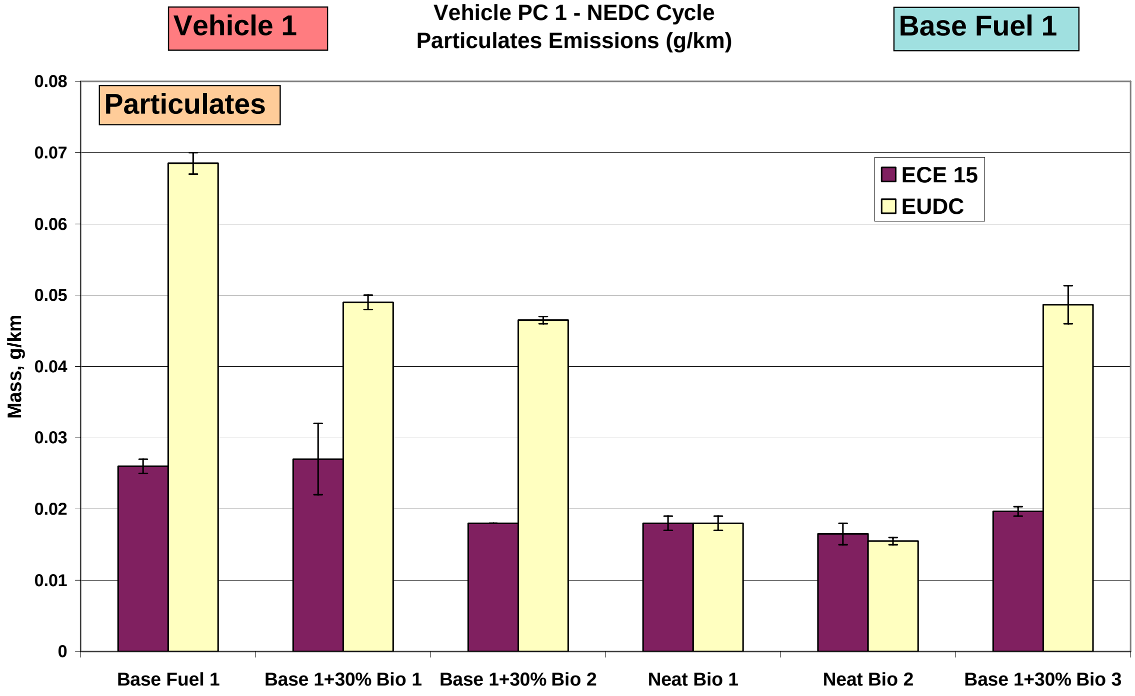


Fig. 23 –Vehicle 2: PM Emissions - combined

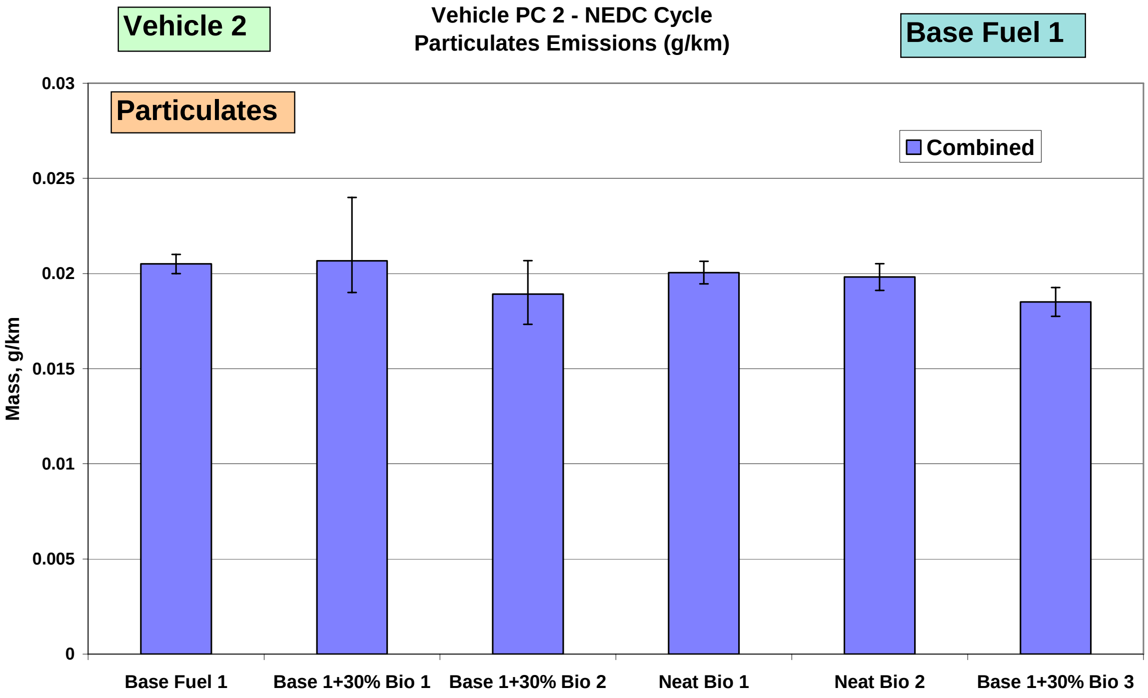
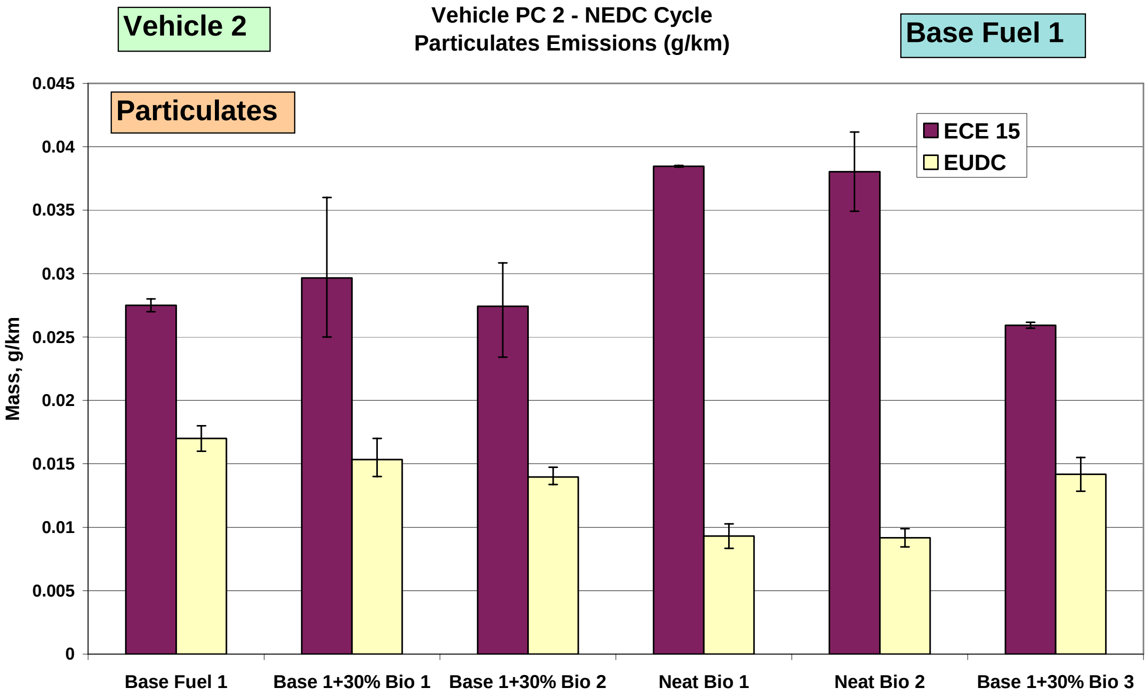


Fig. 24 –Vehicle 2: PM Emissions



4.1.3 Gaseous and Particulate Emissions – Base Fuel 2

The results above described are referred to the Base Fuel 1 that was a standard diesel fuel meeting the EN590 specifications. However, thanks to its properties quite different from the average market values, and for sure, superior to the standard quality, it tends to give better results in terms of exhaust emissions. In particular, the Fuel 1 featured a density close to the lower limit of the density range allowed by the fuel specifications (Directive 98/70/EC) a higher cetane number of the minimum value required. These features influence exhaust emissions and mainly HC and CO ones. In other words, Fuel 1 is a more severe term of reference for biodiesel than the market average fuel quality.

For this reason and to investigate what is the importance of the reference fuel quality it was decided to test, only on the Vehicle 2, also a second Base Fuel having properties more in line with the market average. In table 8, the exhaust emissions of Base Fuel 2 are compared to those of Base Fuel 1; the latter gave significantly lower CO and HC emissions as well as, even if marginally, lower PM emissions.

Table 8 Vehicle 2 -

NEDC -Combined	Base Fuel 1	Base Fuel 2	Differenze %
HC (g/km)	0.032	0.041	+28
CO (g/km)	0.113	0.153	+35
NOx (g/km)	0.453	0.458	+1
PM (g/km)	0.021	0.023	+10%

The emission tests carried out with Base Fuel 1 have been repeated using the Base Fuel 2 and the results are given in table 9 and plotted in the figures 25-32 (the tests performed with the two neat biodiesels were not repeated).

As shown in Tab. 8, Base Fuel 2 gave higher emissions then Base Fuel 1. The percentage variations of emissions noticed changing the base fuel are often of the same order of magnitude or even higher than those noticed when investigating the effect of biodiesel.

The comparison between the results obtained using the Base Fuel 1 and the Base Fuel 2 shows that, from a qualitative point of view, the effect of biodiesel on regulated emissions does not change but in quantitative terms there is a big difference. In fact, compared to the Base Fuel 2, the increases of CO, HC and PM emissions noticed with the fuel containing biodiesel in the case of Base Fuel 1, are noticeably reduced.

It is therefore clear that the quality of the reference fuel is important when the emission performance of biodiesel is investigated.

Table 9

VEHICLE 2	**Base Fuel 2 + 30%Bio 1**	**Base Fuel 2 + 30%Bio 2**	**Neat Bio 1**	**Neat bio 2**	**Base Fuel 2 + 30%Bio 3**
Combined					
HC	-2%	10%	2%	12%	-11%
CO	5%	18%	53%	67%	-6%
NOx	1%	2%	15%	18%	0%
PM	-9%	-1%	-14%	-15%	-10%
ECE 15					
HC	-1%	14%	15%	26%	-10%
CO	5%	19%	55%	70%	-7%
NOx	-2%	0%	11%	14%	-3%
PM	-13%	2%	16%	15%	-7%
EUDC					
HC	-10%	-8%	-58%	-57%	-14%
CO	-1%	1%	9%	3%	-2%
NOx	3%	3%	17%	20%	1%
PM	-5%	-5%	-47%	-47%	-11%

Fig. 25 –Vehicle 2: Hydrocarbon Emissions (Combined)

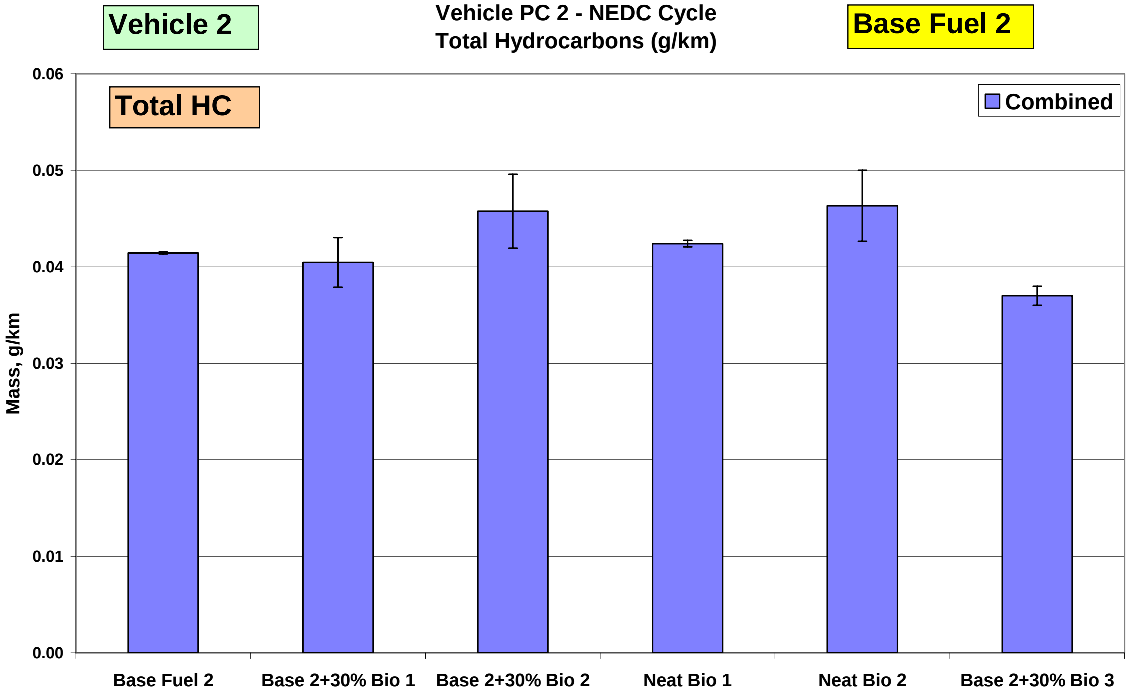


Fig. 26 –Vehicle 2: Hydrocarbon Emissions

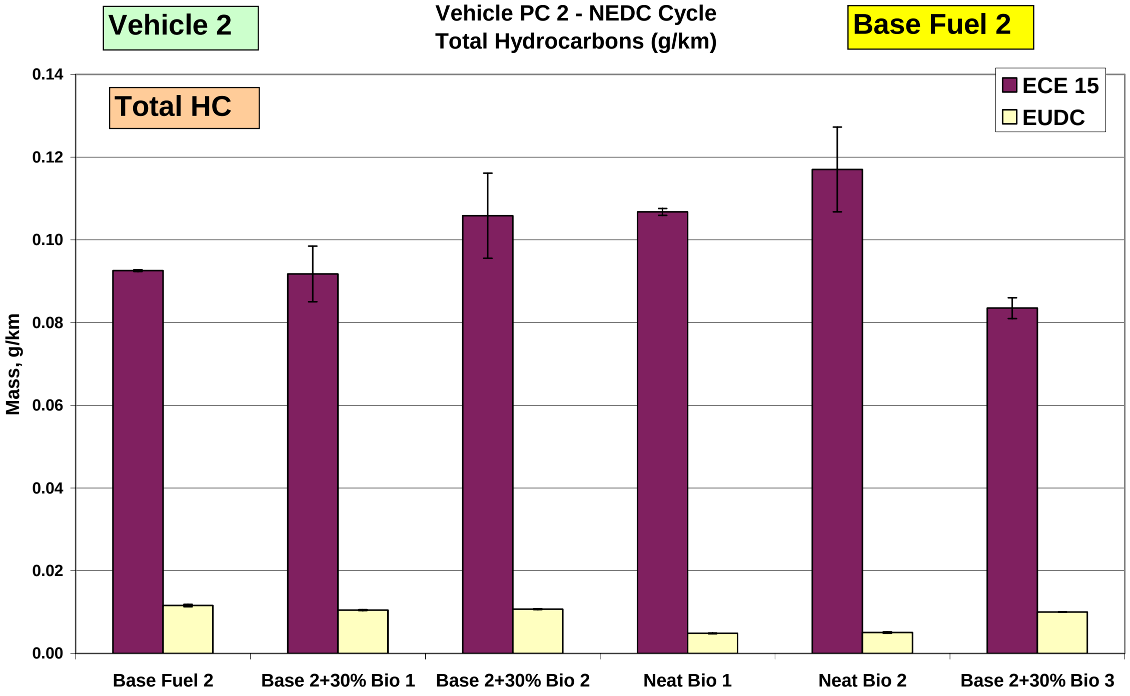


Fig. 27 –Vehicle 2: CO Emissions (Combined)

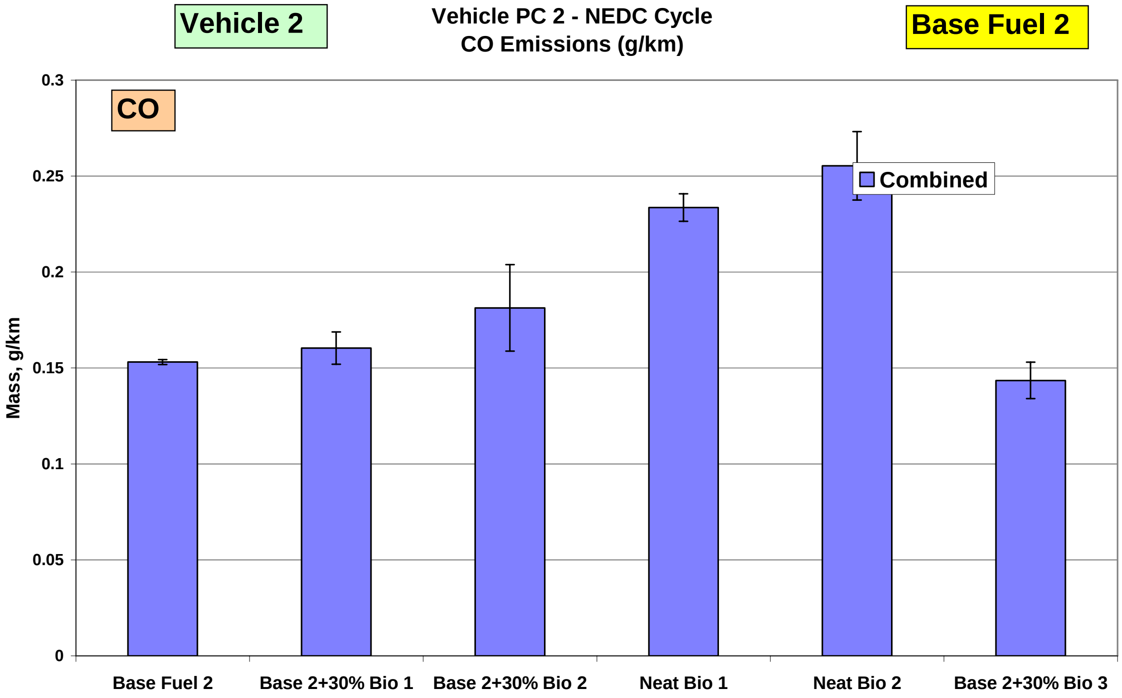


Fig. 28 –Vehicle 2: CO Emissions

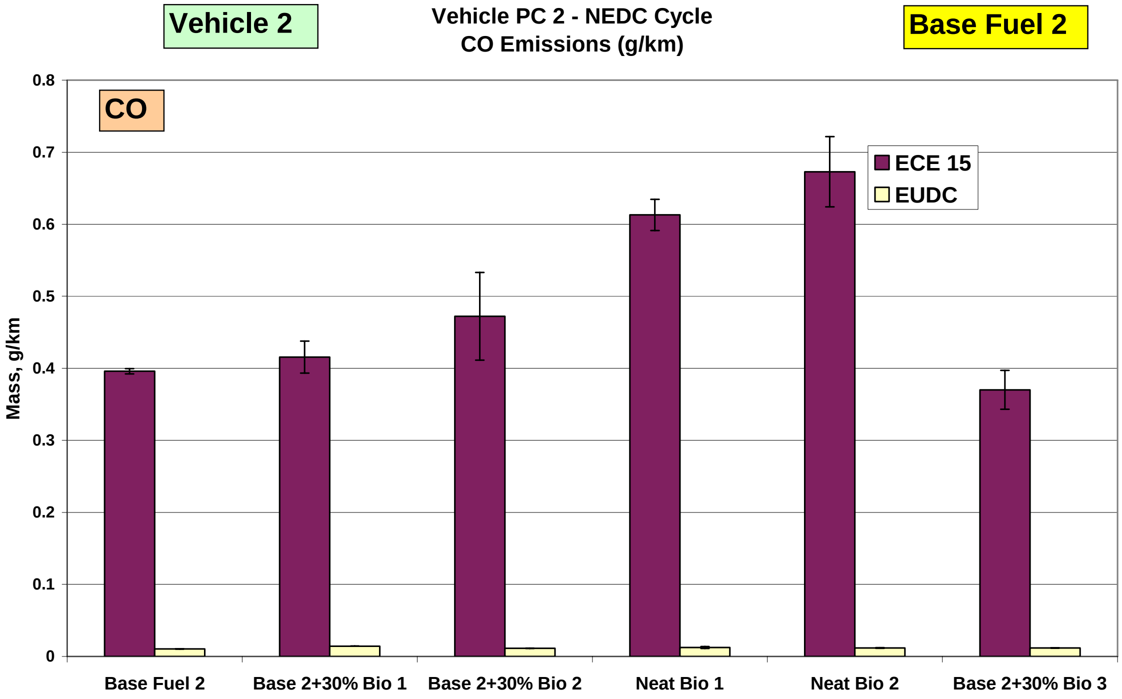


Fig. 29 –Vehicle 2: NOx Emissions (Combined)

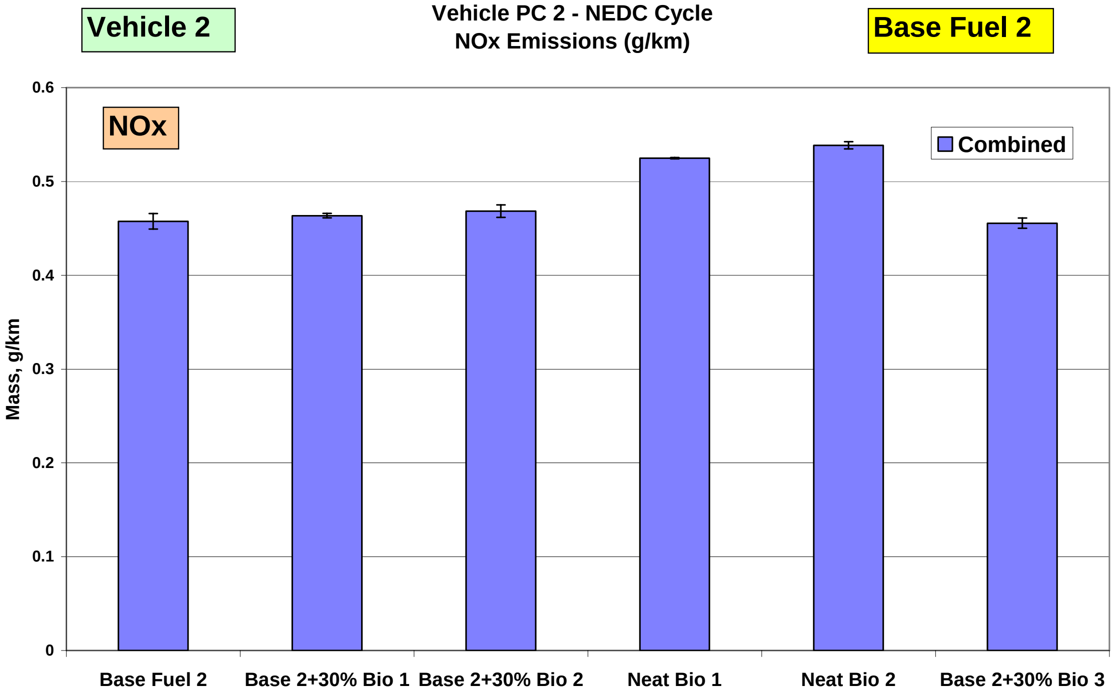


Fig. 30 –Vehicle 2: NOx Emissions

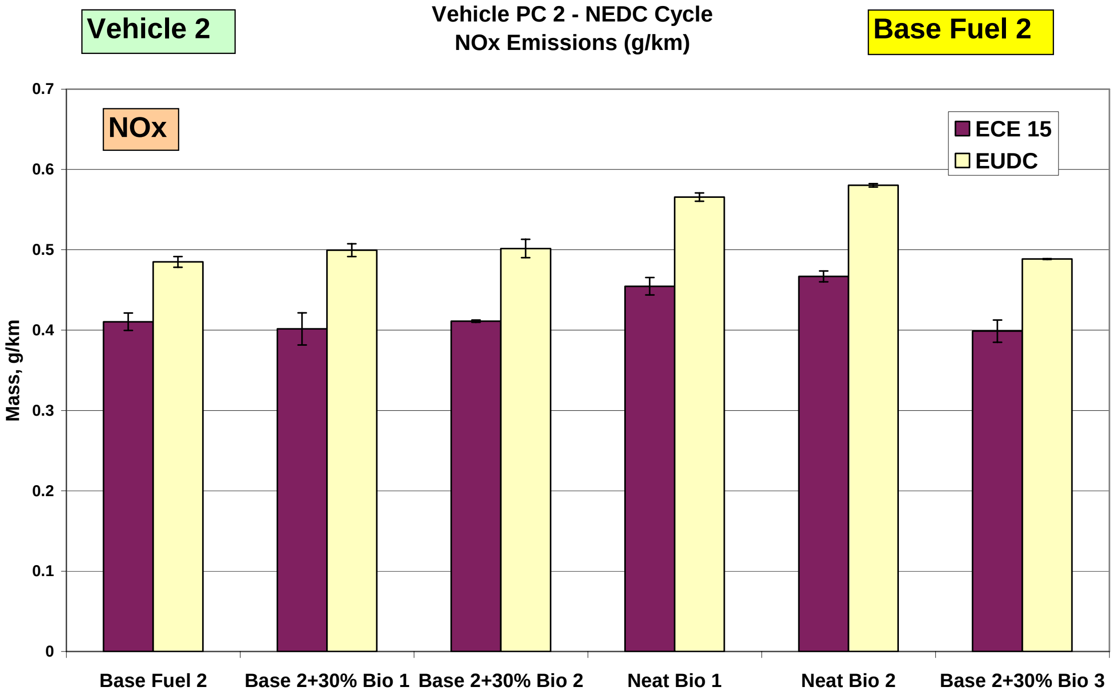


Fig. 31 –Vehicle 2: HC+NOx (Combined)

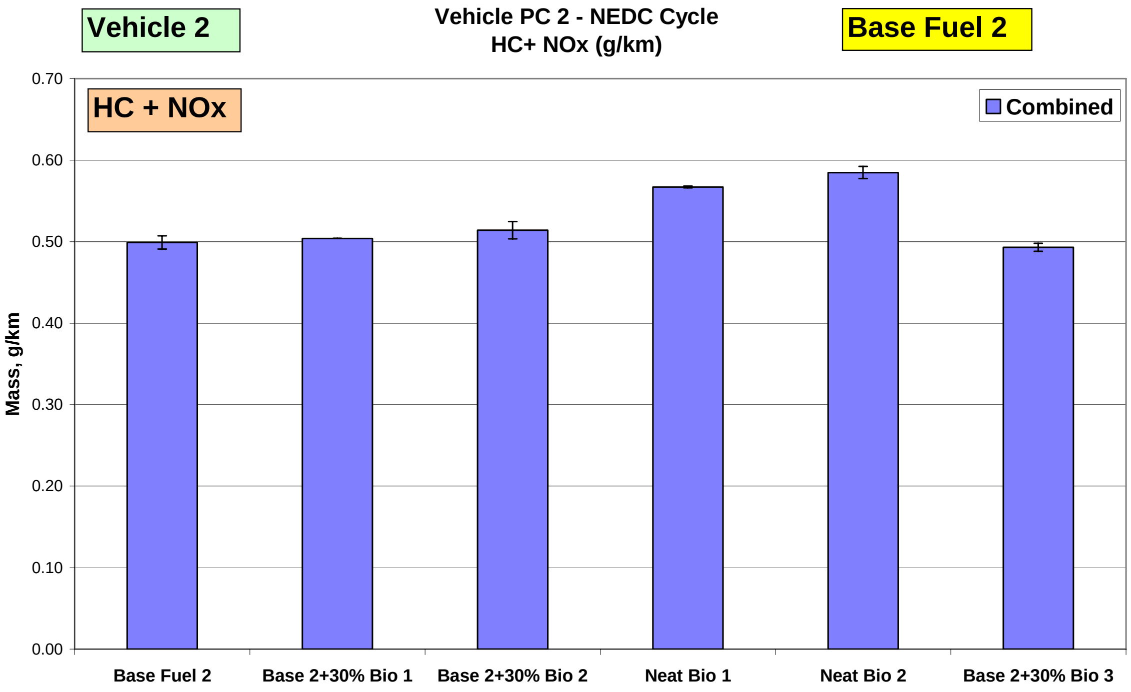


Fig. 32 –Vehicle 2: HC+NOx

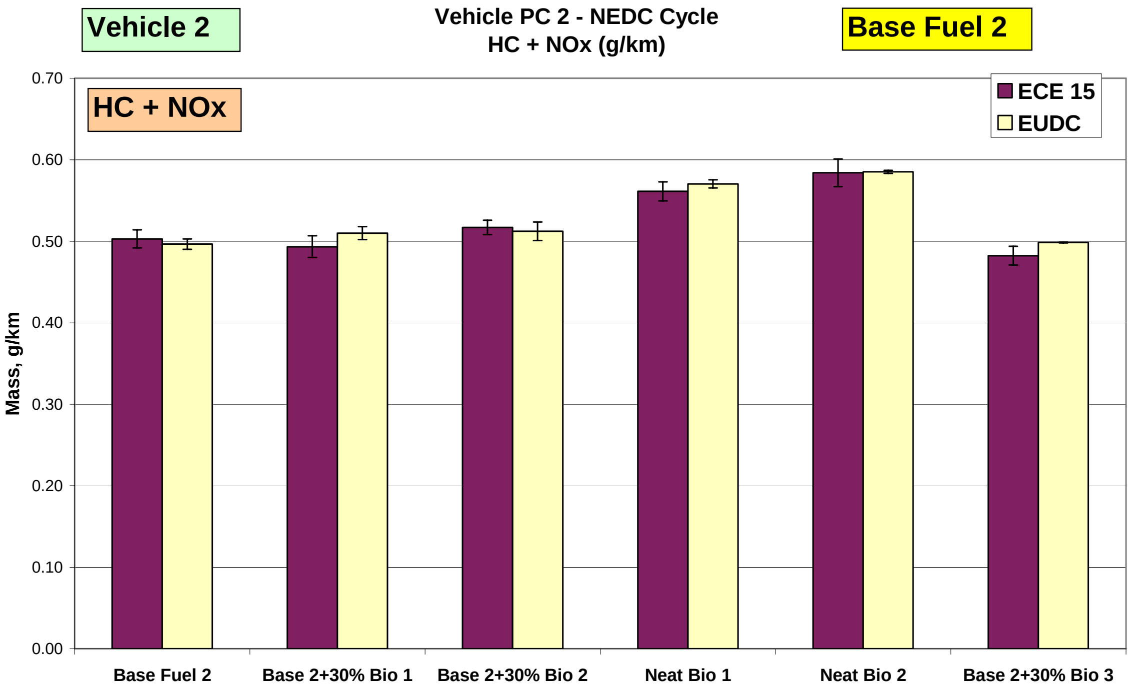


Fig. 33 –Vehicle 2: Particulates Emissions (Combined)

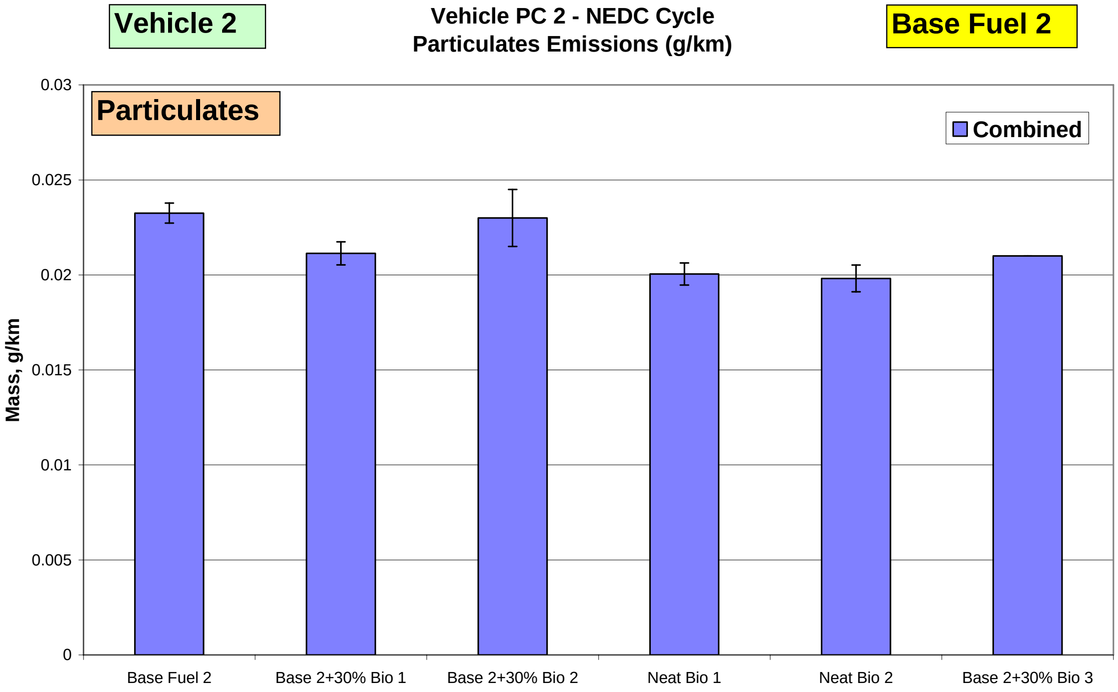
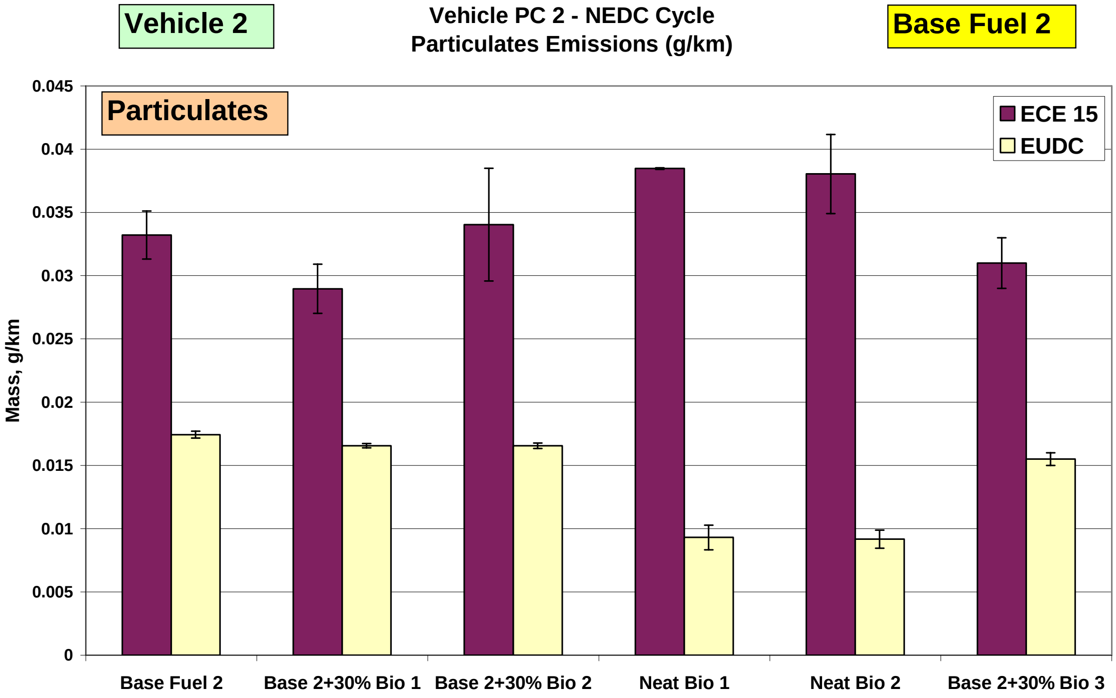


Fig. 34 –Vehicle 2: Particulates Emissions



4.1.4 Modal analysis

During the emission tests the concentration of gaseous pollutants in the exhaust has been recorded continuously and these second by second data can be analysed to better understand the influence of biodiesel on the emissions.
As an example, the figures 35-37 show the concentration of HC, CO and NOx for the vehicle 2 and for some of the test fuels (the base fuel and the two neat biodiesels).

The HC and CO emission profile over the NEDC cycle put in evidence that, as already well known, the major part of these pollutants is emitted during the very first phases of the cycle; it can also be seen that the fuels containing biodiesel give higher HC and CO emissions only during the first 200-300 seconds when compared to the standard diesel fuel. In particular, the largest increase of HC and CO emissions due to biodiesel is concentrated over the first 20-30 seconds.
For example, after the second ECE15 cycle the differences between the standard diesel fuel and the two neat biodiesels are almost negligible.
In other words, the higher CO and HC emissions noticed with the biodiesel occur when the engine is still cold; probably, the different properties of the biodiesel affect to a larger extent the combustion process in this condition rather than when the engine is already warm. In particular, due to the higher boiling point of the biodiesel the evaporation process of the fuel could be much slower when the engine is cold.
Regarding NOx emissions, a different behaviour can be instead noticed: only over the EUDC part of the cycle a significant increase of emission levels can be noticed using the neat biodiesel.

Fig. 35 –Vehicle 2: second by second HC emission measurement

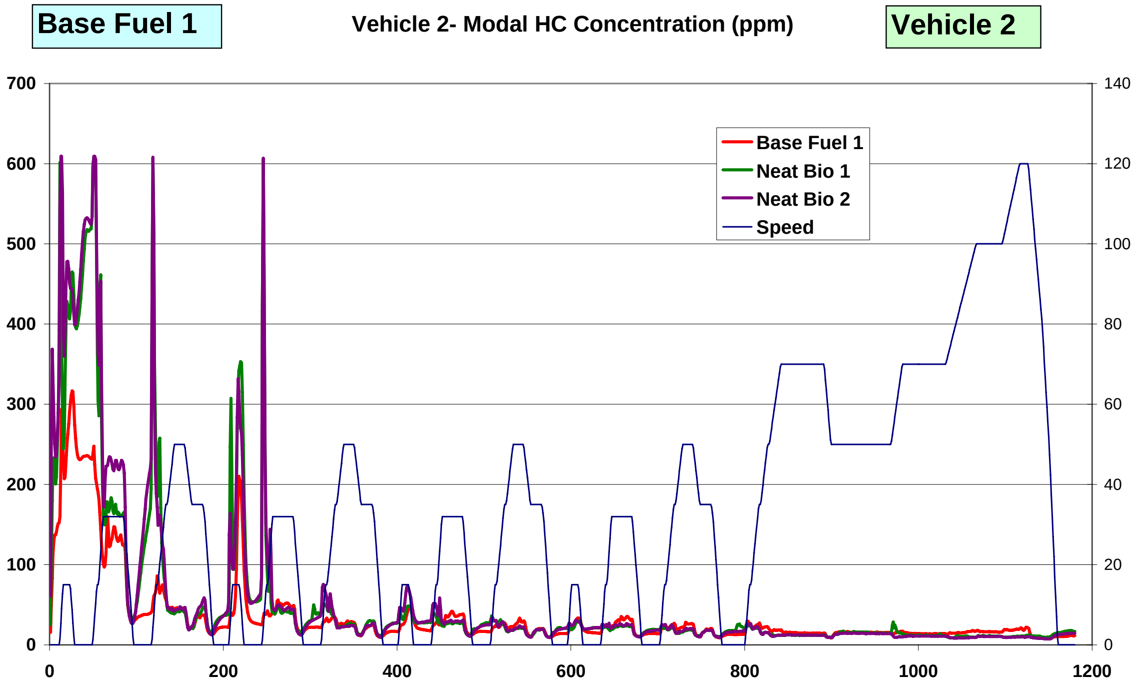


Fig. 36 –Vehicle 2: second by second CO emission measurement

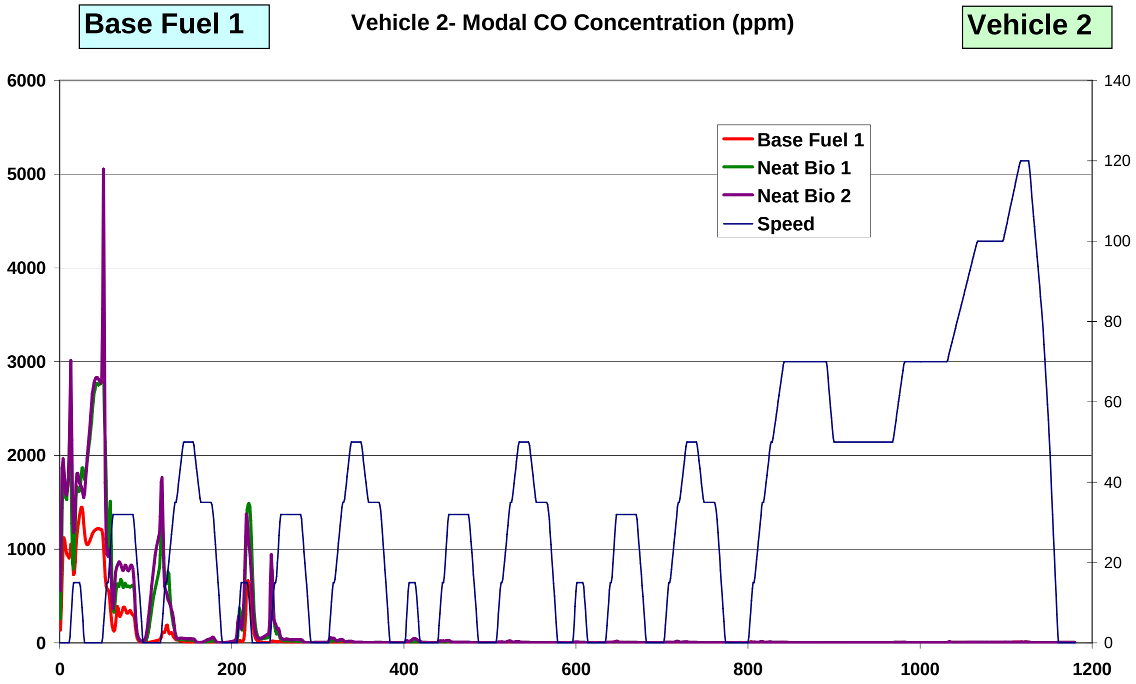


Fig. 37 –Vehicle 2: second by second NOx emission measurement

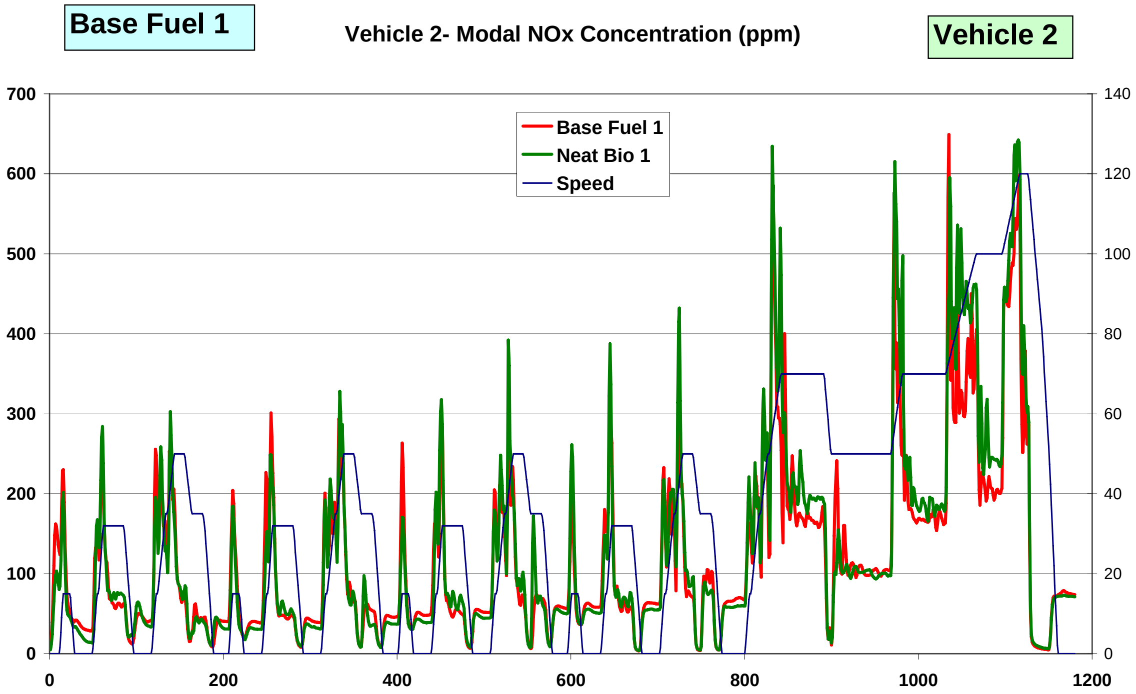


Fig. 38 –Vehicle 2: Emission distribution over the cycle (HC)

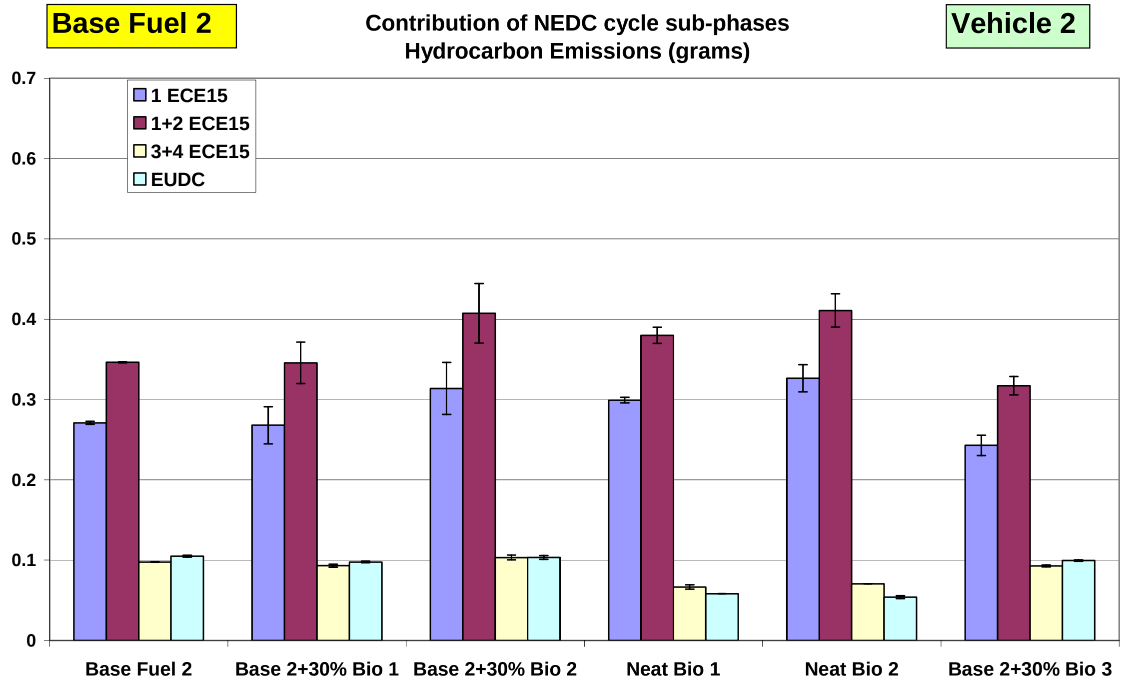


Fig. 39 –Vehicle 2: Emission distribution over the cycle (CO)

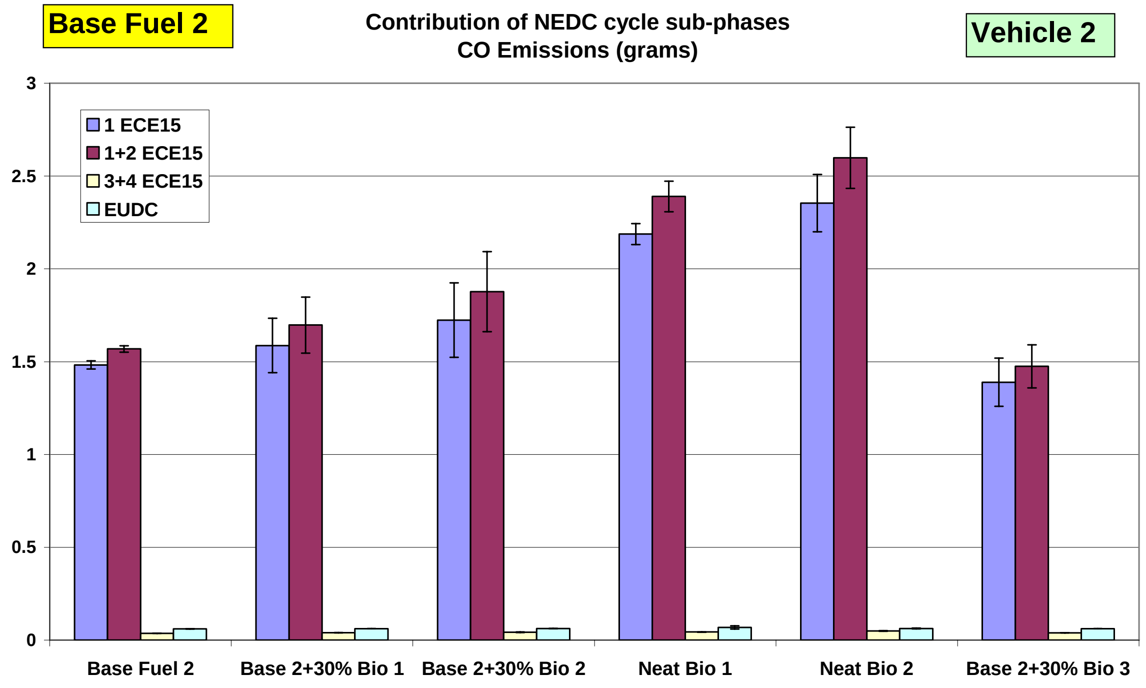
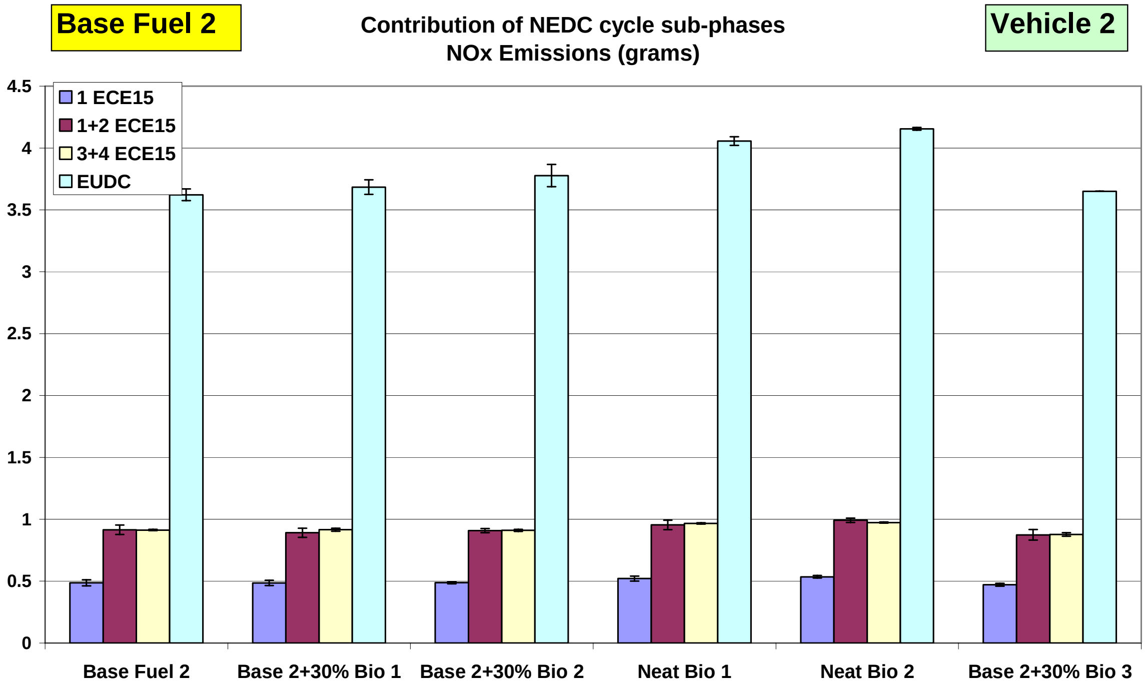


Fig. 40 –Vehicle 2: Emission distribution over the cycle (NOx)



4.1.5 Exhaust temperature

The temperature of the exhaust gas at the outlet of the tailpipe was recorded continuously by means of a thermocouple during each emission test.
The measured temperature profiles obtained with some of the test fuels on the vehicle 2 are shown in the figures ….

The plots show clearly that the exhaust temperature profile, at the tailpipe outlet, was very similar for all the fuels especially over the part of the cycle where the fuels containing biodiesel gave higher emissions. This result suggests that the differences in emissions among the test fuels are not due to a different efficiency of the catalyst that largely depends on the exhaust gas temperature. However this is not conclusive since the exhaust gas temperature upstream the catalyst, directly linked to the catalyst efficiency, was not recorded.

Fig. 41 –Vehicle 1: Exhaust gas temperature (Post-Cat)

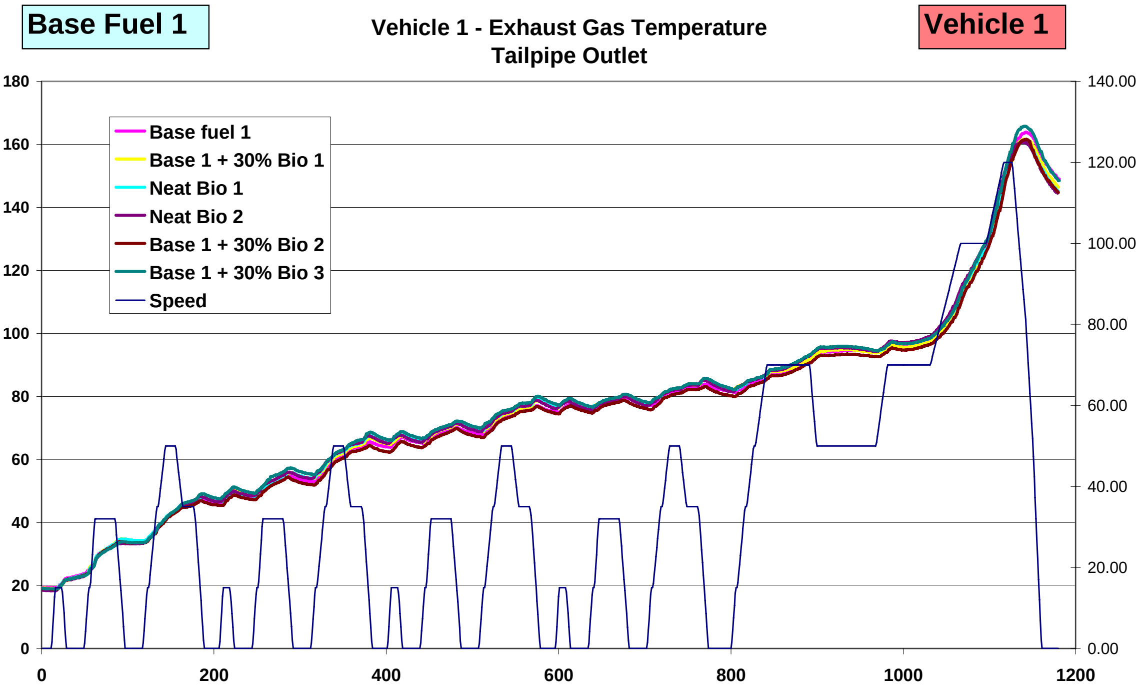
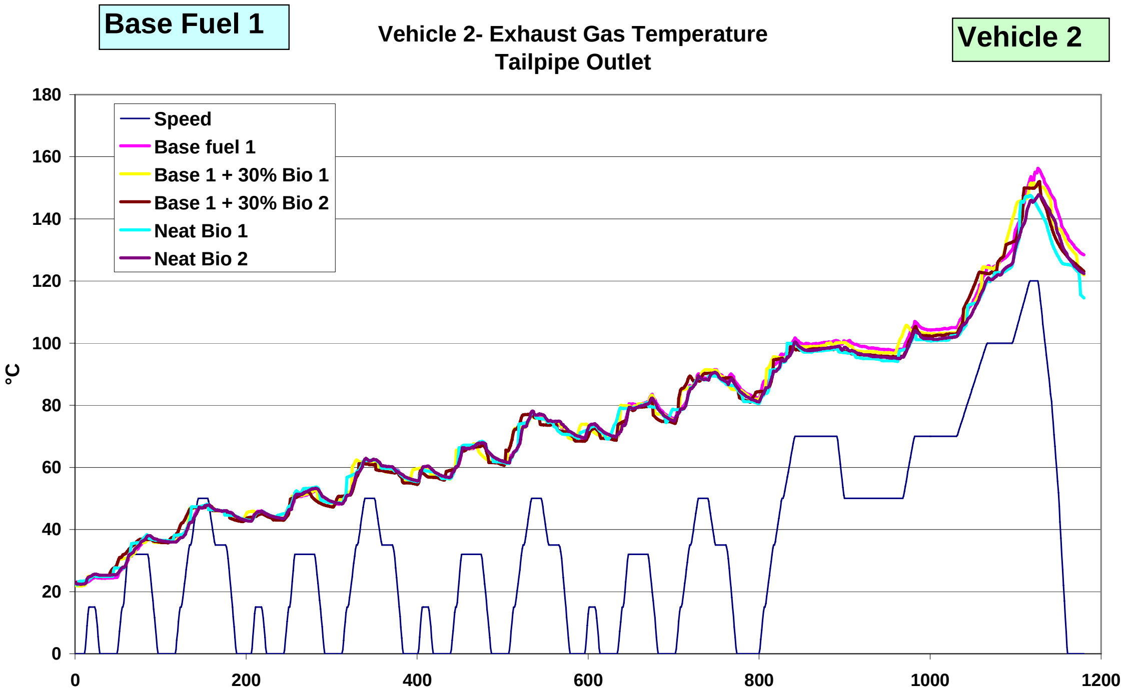


Fig. 42 –Vehicle 2: Exhaust gas temperature (Post-Cat)



4.2 Mass/Size Distribution

The mass/size distributions of particles emitted by the test vehicles were measured by means of a 12 stage Low Pressure Impactor (LPI). The very first stage was a pre-separator; the particle size ranges corresponding to each stage are listed in table …

Stage	**11**	**10**	**9**	**8**	**7**	**6**	**5**	**4**	**3**	**2**	**1**
Aero. Diameter Geom. Mean (nm)	12	25	50	98	194	382	735	1450	2931	5773	11391
Cut-points of each stage (nm)	[8-18]	[18-36]	[36-70]	[70-138]	[138-272]	[272-537]	[537-1060]	[1060-2090]	[2090-4110]	[4110-8110]	[8110-16000]

The results of the measurements performed as previously described are reported in the figures 27-29 (each curve represents the average of two measurements and is referred to the whole NEDC cycle).

The mass collected on each stage has been plotted as a point in correspondence to the geometric mean of the cut-point range of the stage itself. For example, the last stage of the impactor has a cut-point range of 8-18 nm but the geometric mean of this range is 12 nm.

The mass/size distributions of the particles emitted by the two test cars resulted to be very similar; in both cases the largest amount of mass was collected on the 9th stage of the impactor corresponding to a mean aerodynamic diameter of 50 nm and to the range [36-70] nm.
The test fuels containing biodiesel in general did not affect the shape of the distribution with the exception of the two neat biodiesels in the Vehicle 2. In this case it seems that larger particles were emitted by the car as the mean aerodynamic diameter increased.
In all the other cases the reduction of the particulate emission in terms of mass appears to be equally distributed among the stages where most of PM mass emissions are concentrated.

From a quantitative point of view and in terms of total mass, for both the test cars the measurements performed with the LPI are in very good agreement with the results obtained with the legislative procedure (filter method).
In fact, it is possible to calculate the total mass of particulate emitted by the car just adding up the mass collected on each plate of the impactor and compare this value with the one measured using the filter. Obviously, these two mass values are likely to be different, due to both the different filtration/deposition efficiency (that should be lower for the LPI) and the different pressure conditions. In fact, in the last stages of the LPI the pressure is very low because of the high speed of the flow; that could lead to a loss of volatile material due to the dependence of the boiling point on the pressure. Therefore, the total mass calculated from the LPI results is expected to be a bit lower than the one measured with the filter. That is confirmed by the plots 46-48, where these two values are compared.
However, despite the difference between the LPI and the filter value for the total mass, the plots clearly show that the trend of particulate mass against the fuels is exactly the same.`

The comparison between the total mass values obtained with the filter and the LPI gives also some hints on the composition of particulates; as reported in the literature, the SOF (Soluble Organic Fraction) fraction of particulates tends usually to be higher when fuels containing biodiesel are used. As a consequence, considering the loss of volatile material that occurs in the impactor, the

highest difference between the two total mass values should correspond to the use of the neat biodiesels as confirmed by the plots 49-50.
As described in the 4.3 chapter, this result was confirmed by other analysis as well.

Fig. 43 –Vehicle 1: PM mass size distribution

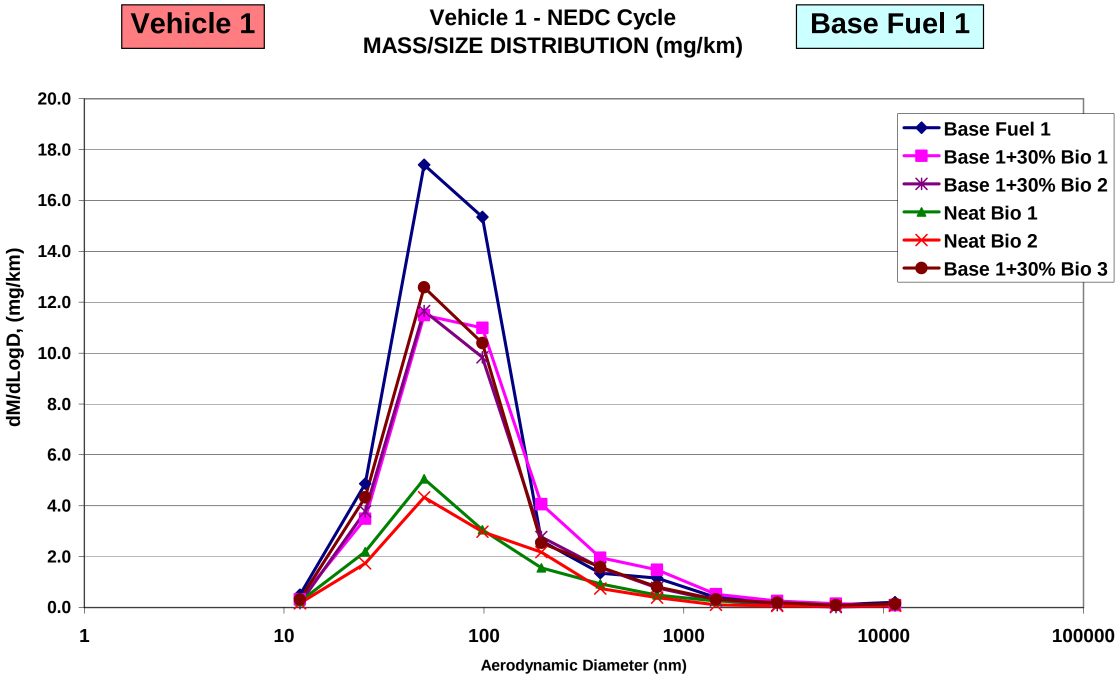


Fig.44 – Vehicle 2: PM mass size distribution (Base fuel 1)

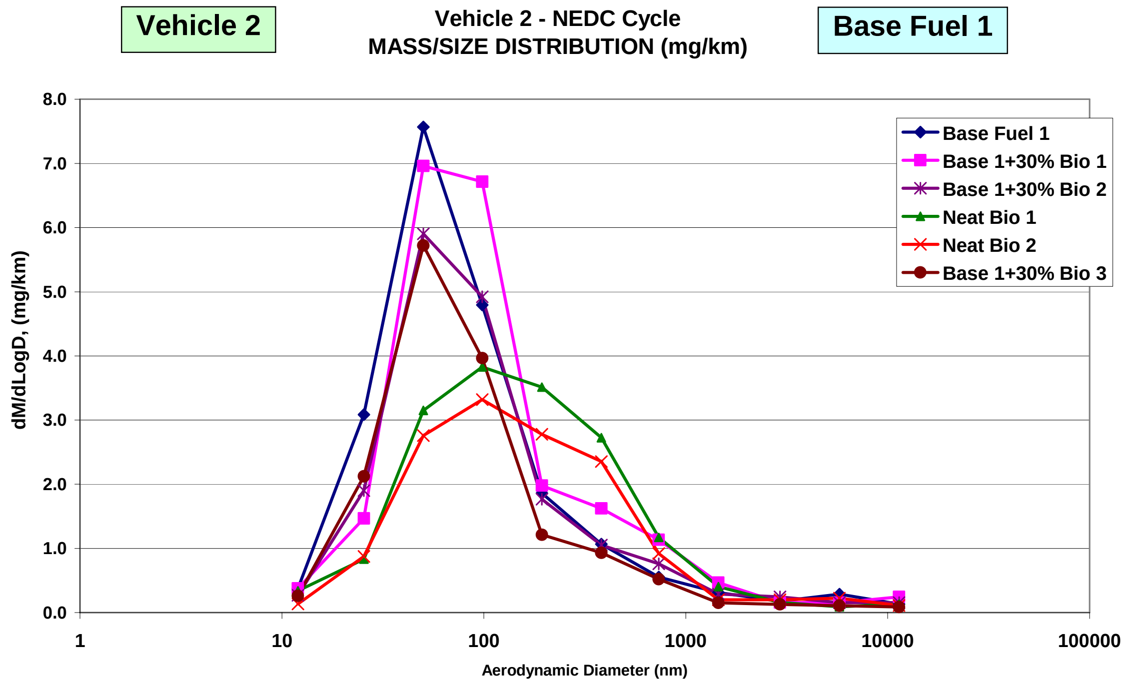


Fig.45 - Vehicle 2: PM mass size distribution (Base fuel 2)

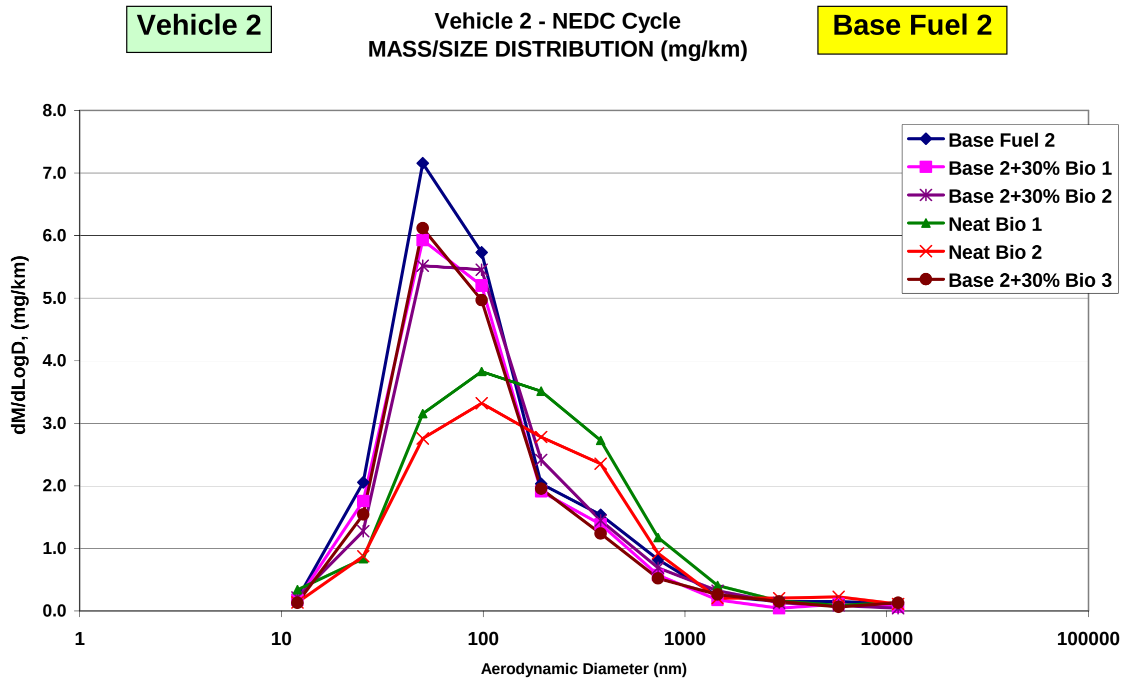


Fig. 46 – Comparison between the total mass measured with the filter and the LPI (Vehicle 1)

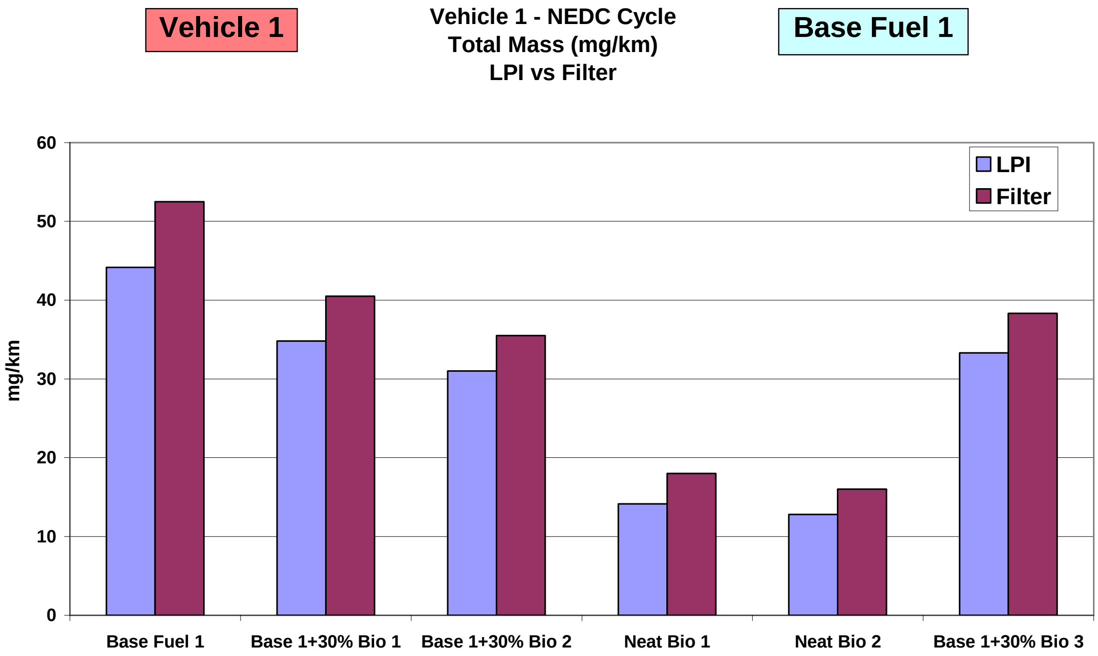


Fig. 47 – Comparison between the total mass measured with the filter and the LPI (Vehicle 2)

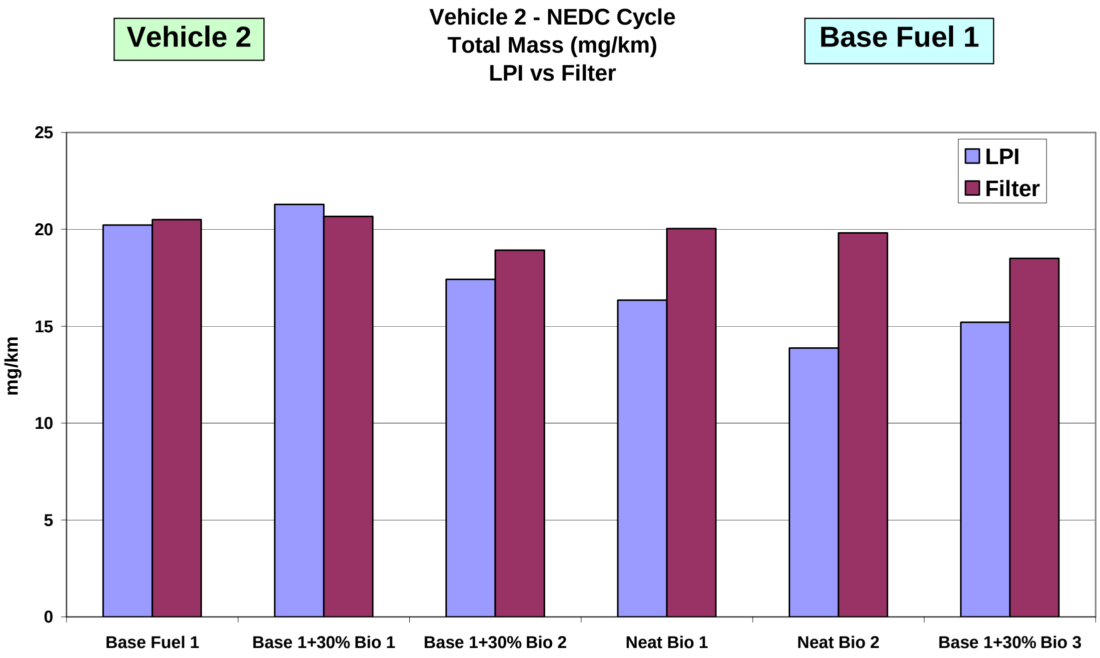


Fig. 48 – Comparison between the total mass measured with the filter and the LPI (Vehicle 2-Base fuel 2)

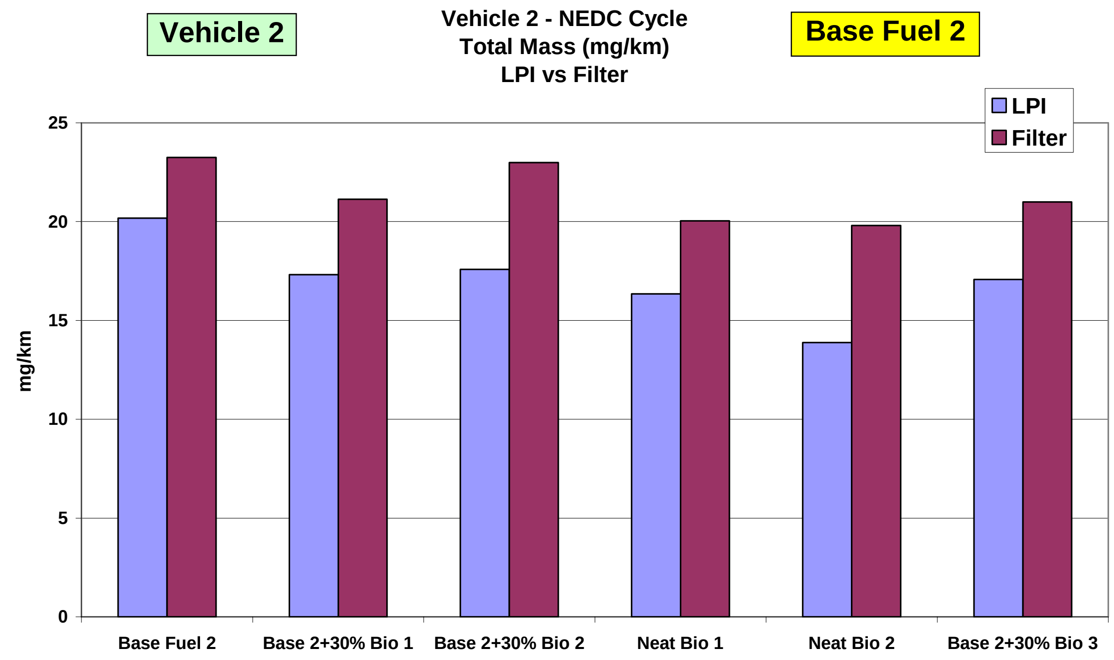


Fig. 49 – Difference (percentage) between the total mass measured with the filter (base line) and the LPI

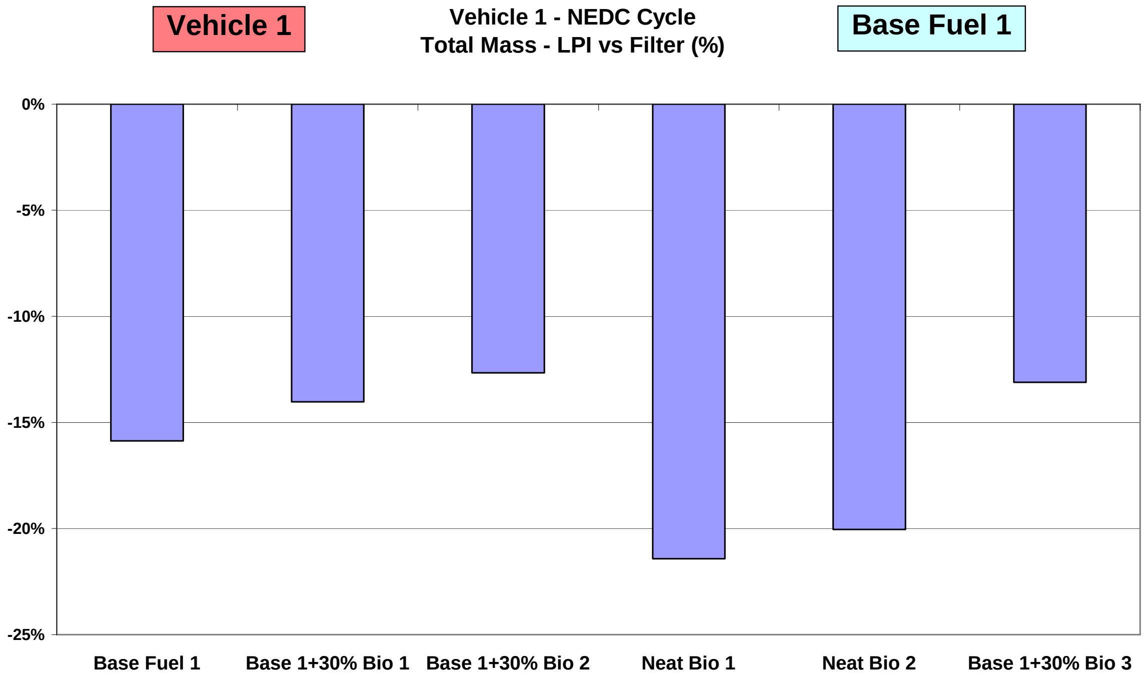


Fig. 50 – Difference (percentage) between the total mass measured with the filter (base line) and the LPI

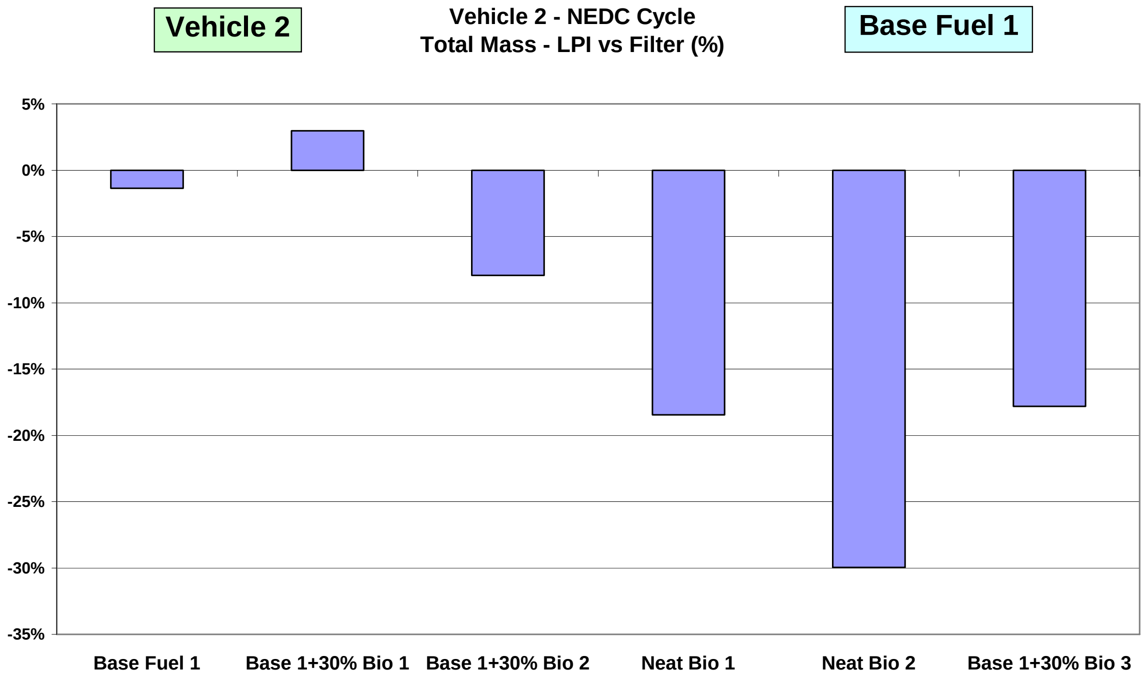
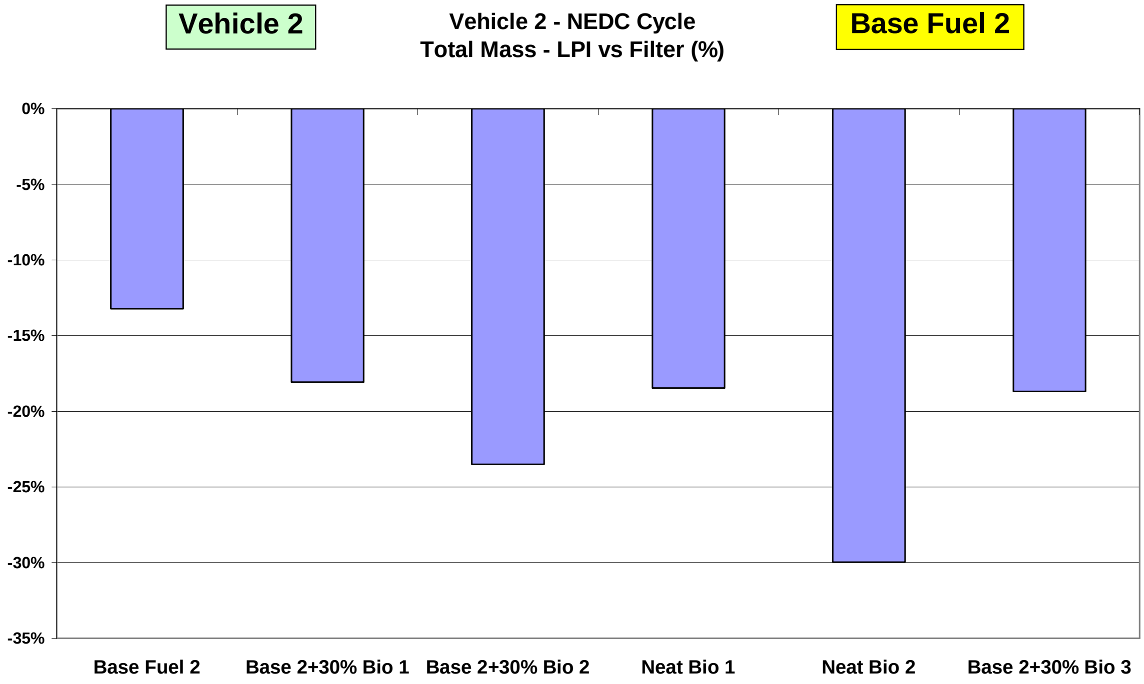


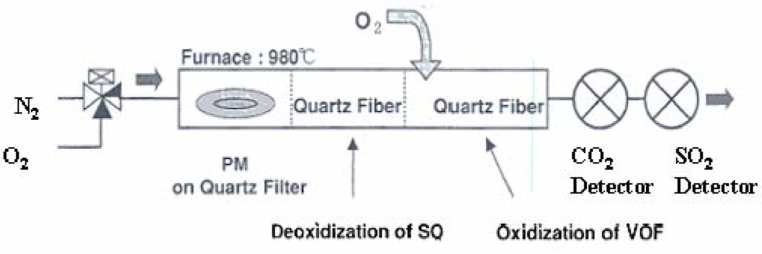
Fig. 51 – Difference (percentage) between the total mass measured with the filter (base line) and the LPI



4.3 Composition of particulates: “soot” and “SOF” fractions

The composition of the particulate matter was investigated splitting the mass collected in the soot and SOF fractions using a special equipment, the MEXA-1370 PM produced by Horiba. That was done only for the Vehicle2 and just for the Base Fuel 1.

The MEXA-1370 PM can measure the main particulate fractions (soot, SOF, sulphates) separately by detecting the CO2 and SO2 gas that are generated from vaporization, oxidation and reduction processes of filtered PM samples.
The first step of the measurement consists in putting a sample filter into a combustion furnace at 980 °C where N2 gas flows as a carrier. Under these conditions the volatile organic fraction of PM is completely vaporized and then oxidized into CO2 by O2 gas supplied into a dedicated compartment of the furnace. Thus SOF mass can be calculated by measuring the amount of CO2 generated in this process. After completing the vaporization of the organic carbon fraction, the carrier gas is switched to O2 so that the elementary carbon is converted into CO2 by combustion. Soot mass can be calculated from the amount of Co2 generated at this stage. Sulphates are also vaporized and converted into SO2 at the same time: similarly, the sulphate mass can be calculated by measuring the amount of SO2.



Schematic configuration of the MEXA-1370PM

When this analysis was performed on the particulate samples collected in the emission tests carried out with fuels containing biodiesel, it appeared clear that the instrument was optimised for particulate emissions obtained from vehicles fed with conventional diesel fuels. In fact, it was noticed that the period of time was too short to completely vaporize the volatile material adsorbed on the soot fraction of those samples. As a consequence the repeatability was quite poor and probably, the SOF fraction was underestimated.

Despite this problem, the results that have been obtained show clearly that with biodiesel the soot fraction is reduced noticeably while the SOF fraction is significantly increased.

Fig. 52 – Particulate composition

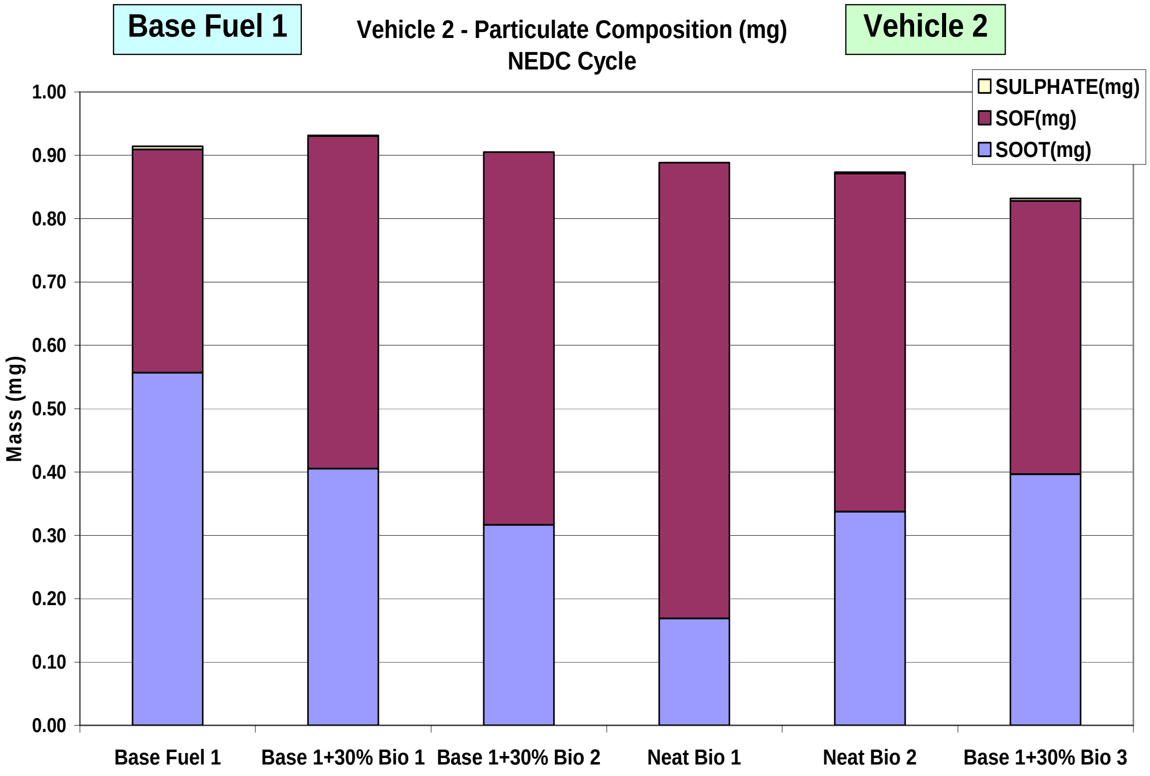
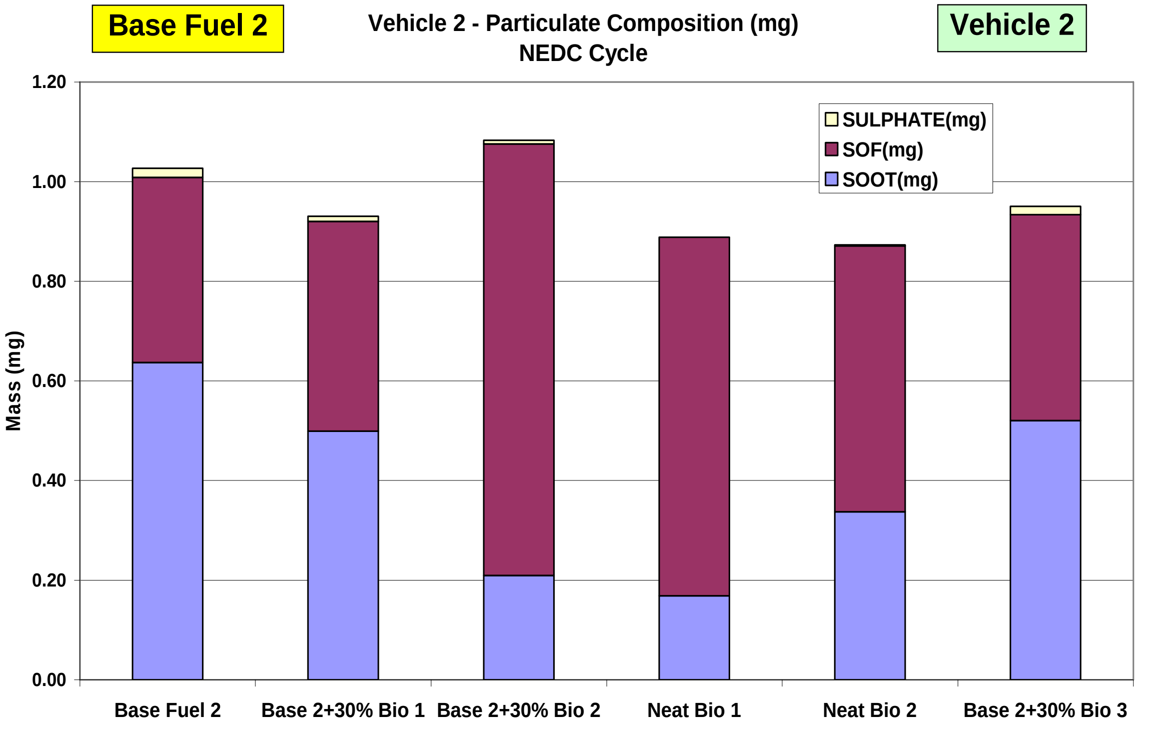


Fig. 53 – Particulate composition



4.4 Unregulated emissions: Chemical composition of particulate and Volatile Organic Fraction of the vehicular exhaust.

The research activity at the JRC-TRANSPORT & AIR QUALTY Unit is not only heading for the physical characterization of the particles emitted by vehicles but also concerned in the investigation of the Chemical composition of such emissions, their toxicity and their contribution to air pollution and health risks.

The European Commission and the European Parliament have been time ago persuaded through the establishment of the Clean Air for Europe Programme and in the last few years, new Daughter Directives have been put forward with new limits in the air for several pollutants. The Third daughter directive relating with Ozone (2002/3/EC) and the Fourth Daughter directive that covers the remaining pollutants listed in Annex I of the 96/62/EC Directive on Air Quality: As, Cd, Ni, Hg and benzo(a)Pyrene (2004/107/EC)

Following this demand from the European legislation one of the major challenges for the transport sector is to reduce particulate emissions from diesel vehicles in order to meet future emission standards and to reduce their contribution to the pollution of ambient air minimizing in such way the risk for the human health.

Challenges for the improvement of the air quality in Europe arrive to the research field, not only from the technological point of view but also from the research on alternative fuels. In short, the biofuels have been presented as a possible and feasible alternative for the automotive sector. Quite a few studies have been carried out on heavy duty engines and, moreover, sometimes they have come to contrasting conclusions. The situation is even more complex when unregulated emissions are considered, (i.e. PAHs adsorbed on particulate). Some works have shown an increase of PAHs emissions while in other cases all emissions resulted to be lowered by the use of biodiesel.

By means of the experimental procedure described in this report, a significant number of non regulated, potentially toxic compounds, namely PAH and Azaarenes derivatives, as well as Ozone precursors have been identified. The concentrations of the compounds which have been quantified in this study are in the same range of those found either in the literature or in the emissions from similar fuels and technologies.

In the following pages, we show the results coming out from the c**hemical analysis of PAH derivatives adsorbed in the Exhaust particulate** (4.4.1) as well as the equivalent toxicity referred to B(a)Py**.** Quantization of PAH and Aza-PAH derivatives, in terms of mass per km, is exposed too. It is also presented the levels of Volatile organic compounds in the gas phase of the vehicle exhaust and their contribution to atmospheric Ozone formation (4.4.2)

4.4.1. Chemical Analysis of PAH derivatives adsorbed in the Exhaust particulate: Experimental Procedure

In order to quantify a number of selected PAHs and azaarenes adsorbed on particulate, PM was collected on standard Teflon coated filters according to the EU current regulated procedures for Total Mass. Filters were then extracted and evaporated, went through a clean-up procedure, were evaporated again nearly to dryness, dissolved in toluene and finally analyzed by gas chromatography-mass spectrometry (GC-MS).

Among the organic compounds adsorbed on particulates, the present study focused on the detection of sixteen PAH (Polyaromatic hydrocarbons) and thirty-two Azaarenes (only 6 were found), since there is evidence of the carcinogenicity for these compounds.

The method used in this work has been developed in our laboratories and it is based on the EPA method TO 13 and ISO/DIS 12844.

Fig. 54 Filter extraction, evaporation, clean-up and GC-MS analysis

This method applies well to particulate collected on filters from vehicle exhaust, motorcycle exhaust, etc.

Total particulate mass was measured using Pallflex 70 mm T60A20 filters which were weighed before and after the emission test. The particulate collected on these filters commonly consist on agglomerates of very small carbon particles (soot fraction) and heavy hydrocarbons adsorbed on them (soluble organic fraction). Chemical composition of the soluble organic fraction is important due to its potential relevance for human health. In particular, what it is grabbing our attention is the amount of potentially harmful organic compounds adsorbed on the particles.

After the sampling, the filters containing the particulate matter were extracted in an automatic Soxhlet extractor for 2 h with dichloromethane. The extracts were evaporated nearly to dryness with a "Turbo Vap" System operating at 40°C. After reducing the volume, the extracts were transferred in a SPE column for the clean-up procedure. The residue, including PAHs and azaarenes, were passed through a "PAHs soil" solid phase extraction cartridge (J. T. Baker). After removal of non-polar species by elution with hexane a second fraction eluted with dichloromethane/hexane (60:40) and successively with acetonitrile/TEA. Both the second and third fractions were collected together. The eluate was evaporated almost to dryness and redissolved in toluene and analyzed by GC-MS.

GC-MS analyses were performed with a HP 6890 Series Plus GC system equipped with an auto-injector HP 7683 Series. The mass spectrometer was a 5973 HP Mass Selective Detector equipped with both Electron Impact and Chemical Ionisation sources. The column used was a HP-5MS fused silica capillary column, 30 m, 0.25 mm inner diameter, 0.25 μm film thickness.

Separation conditions used: injection volume 2 μL in pulsed splitless mode; helium carrier gas at a constant flow rate of 1.0 mL/min; injector temperature 280°C. Run time for one analysis was 36.5 min. EI ionisation was employed at 70 eV. MS source temperature was set to 230 °C; MS quadrupole temperature: 150 °C and GC/MS interface temperature: 280 °C

4.4.2. VOC speciation of the gas phase fraction of the exhaust

4.4.2.1. Experimental details

Ten liters of vehicle exhaust sample, withdrawn from the dilution tunnel, were collected in Tedlar™ bags. A 2D–Gas Chromatograph (2D-GC) equipped with dual flame ionization detector (FID) is used for the determination of the C_2-C_9 ozone precursor hydrocarbons specified in the Ozone Directive 2002/3/EC.

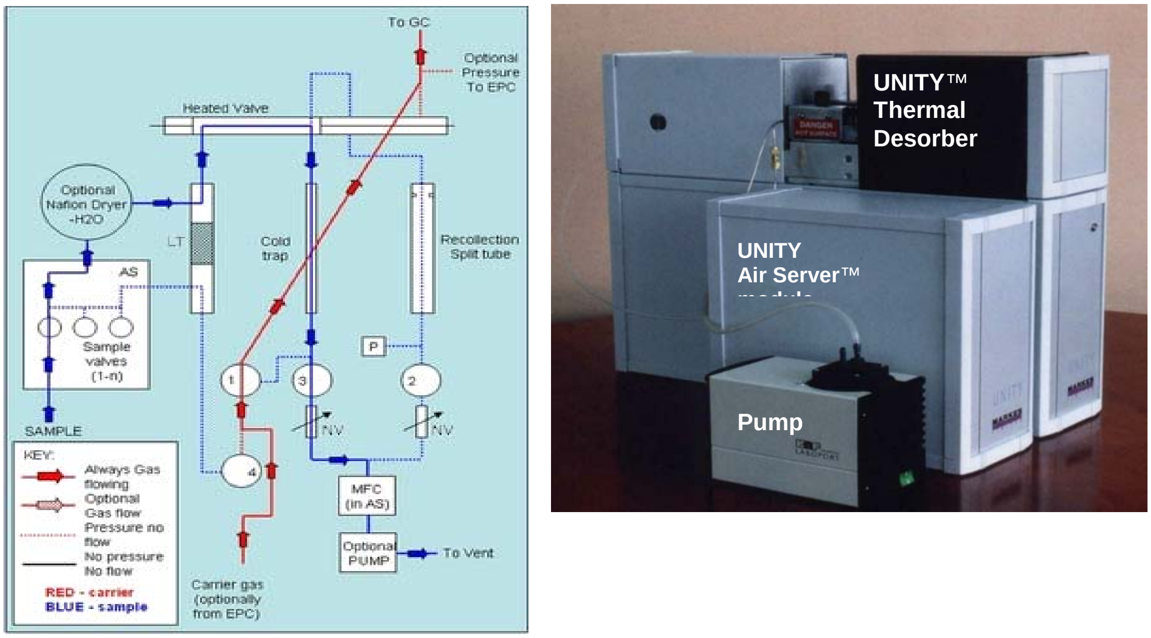
Figure 55 – Chromatography analysis (2D-GC)

The Tedlar™ bags containing the exhausts are connected to the analyzer inlet. Only a limited sample volume of 80 ml (20 ml/min for 4 minutes) was collected and analyzed for each driving test, allowing replicated analysis if necessary. A thermal desorption unit (UNITY™) and an auxiliary sampling device (Air Server™) from Markes International (Pontyclun, UK) are used to collect samples from the Tedlar bags of exhaust gases.

Samples are transferred to a multilayer adsorbent trap (Markes) that operates at -15°C. The trap is then heated up to 320°C and a whole-sample thermo-desorption / injection step follows. The released compounds are injected into the gas chromatograph via a heated transfer line (130°C) lined with uncoated, deactivated fused silica.

Analysis were performed with a gas chromatograph (6890, Agilent, Wilmington, DE, USA) equipped with a “Deans switch” followed by a two column system with a dual flame ionisation detector (FID) [12].

Figure 56 – Thermal desorption unit *(Photo by courtesy of MARKERS ltd).*

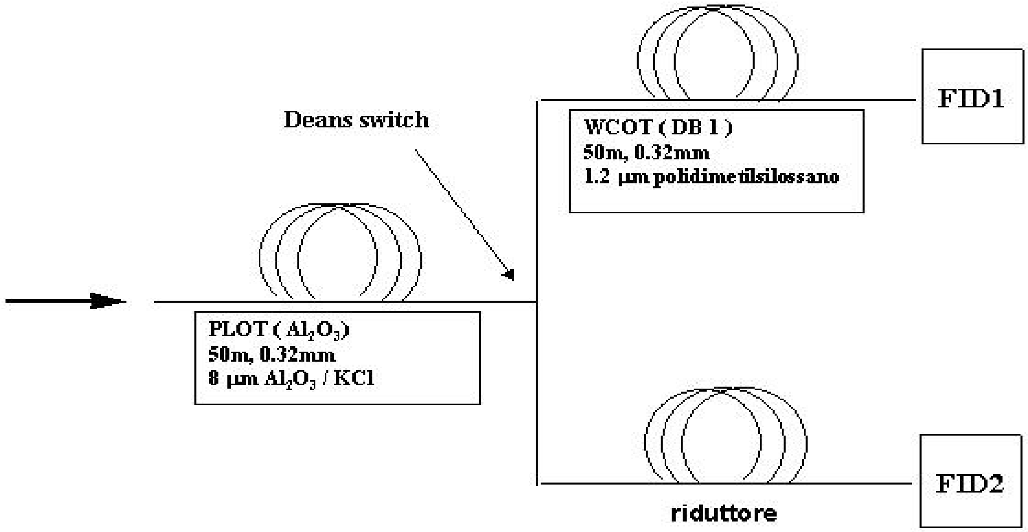


LT: connection tube
1-4 : solenoid valves
P : pressure transducer
MFC : mass flow controller
NV : needle valve

All the effluent, transferred to the gas chromatograph, is directed into the first column (“PLOT” 50m×0.32mm, coated with Al_2O_3 / KCl, 8µm). For the first 15 minutes the C_2-C_5 compounds elute from this column and are sent, via the “Deans switch”, towards FID 2. Afterwards the “Deans switch” activates directing the C_6-C_9 fraction into the second column (“WCOT” 50m×0.32mm, coated with polidimethyl-siloxane, 1.2 µm) and then to FID 1. From this point on, two chromatograms are produced in parallel: one on each FID.

The two columns work with the same program of temperatures: isotherm at 40°C for 2 minutes, ramp at 7 °C/min, isotherm at 120°C for 3 minutes, ramp at 7 °C/min, isotherm at 200°C for 35 minutes. The carrier gas is Helium.

Fig 57. "Deans switch" followed by two column system with a dual flame ionisation detector (FID)



VOCs emissions (g/km) are calculated as follows:

$$Mvi = \frac{Cvi \cdot PMi \cdot Vtot}{D \cdot d \cdot 1000}$$

Mvi = mass of VOCi emitted expressed as g/Km
C_{vi} = concentration of VOCi expressed as ppm
Pmi = molecular weight of VOCi (g/mol)
$Vtot$ = Vmix + V_{PM} + V_{LPI} (m^3)
D = 24 mol/l
d = distance in km

We end here a short description of the methodology followed at the JRC-TAQ Unit. By means of this experimental procedure, a significant number of non regulated, potentially toxic compounds, namely PAH and Azaarenes derivatives, as well as Ozone precursors have been identified by mean of the experimental procedures just described. The concentrations in which these compounds have been quantified are in the same range as we have found in the literature or in emissions from other similar fuels and technologies.

4.4.3. PAH concentration in the particulate exhaust of LD vehicles fuelled with biodiesel

As we have anticipated before, biodiesel has been widespread investigated in diesel engines looking for the regulated pollutants. There is no question about the fact that biodiesel fuel blends with less that 20% biodiesel have a potential to reduce the emission of PM, CO and HC and so they can be pointed as an alternative to diesel fuel without significant changes in existing engines. However the emission of PAHs and their carcinogenic potency (BaP_{eq}) have seldom been addressed in LD vehicles. What we present bellow are results that illustrate the behavior of some, blend or neat biofuels, regarding PAH content of the exhaust in two different LD vehicles.

For all PAHs measurements, the concentration values are expressed in µg/km and we always report two values corresponding to both parts of the cycle: UDC and EUDC. The total PAH concentration we are referring is the sum of the concentrations of 14 PAH components, all of the included in the EPA standard for Polyaromatic compounds.

Fig. 58 Total PAH emissions: vehicle 1

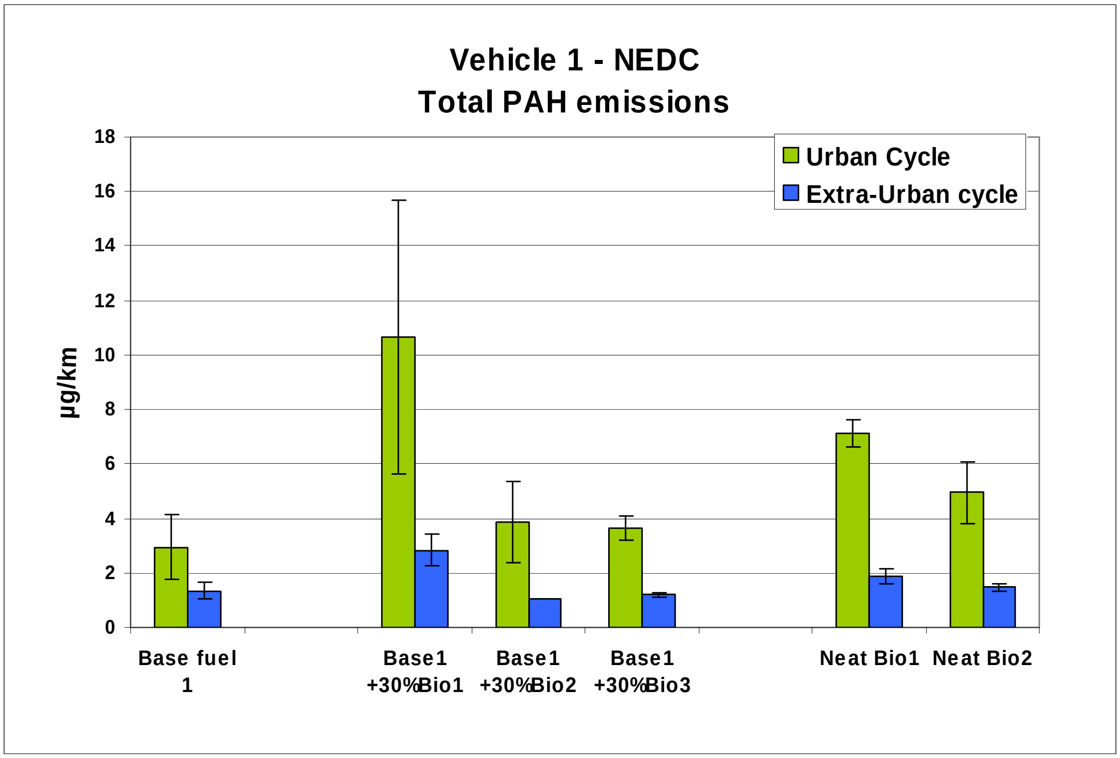


Figure 58 shows the variation of PAH emissions (µg PAH/km) of the exhaust obtained for the 1st vehicle running the European Driving Cycle. This vehicle was fueled with six different fuels: commercial diesel reference fuel, two neat biodiesel fuels and 3 blended fuels including 30% of biodiesel. We received two filters for each test, one for the UDC phase and another one for the EUDC phase, which were analyzed for their chemical composition following the procedure described before. Each test was repeated for verification and the results in figure 58 show the average ± 95% confidence interval for the 6 fuels tested.

First fact which comes out from Figure 58 is that for all test and fuels, either pure or blended, we have found that total PAHs emissions are much higher for the UDC than for the EUDC. This result is very predictable since the amount of unburned PAHs should be higher during the cold part of the cycle when the combustion is expected not to be as proficient as in the second part of the cycle. Throughout the UDC phase of the cycle the concentrations were always very low and they varied from 1.1μg PAH/km, emitted by Base fuel 1 plus 30% of Biodiesel 2, to 2.8μg PAH/km for Base fuel 1 plus 30% of Biodiesel 1.

Second most important information we observe in this graph regards the values of total PAH emitted during the urban phase of the cycle (UDC values). When the car is fueled with biodiesel, either blended at 30% or neat, we always detected higher values than for the reference fuel during the UDC part of the cycle. This finding may be due to the increase of SOF fraction in the PM emitted by Biodiesel fueled cars, when running in urban context [26, 42]. As we have shown in previous pages (Fig 52: Soot vs. SOF results) the soot fraction of PM is notably reduced with biodiesel while the SOF fraction is significantly increased. This fact makes that results showed in figure 58 should not be shocking since the soluble organic fraction (SOF) is mainly formed by heavy hydrocarbons from unburned fuel and lube oil condensed and/ or adsorbed on the carbon particle. The reason for this incomplete combustion has to do with the fact that the combustion of biodiesel fuels is not so complete in engines operating at low engine loads and speeds unless the injection process is settled properly for the different density of the neat or blended biofuels. A good injection quality must be ensured for these fuels if we like to optimize the combustion process and any variation in the properties of the fuel may directly affect the efficiency of the injection and so the combustion. This fact also explains the results observed when Neat biodiesel is used for fueling the vehicle 1. Once again, the emissions increase if compared with the Base fuel 1 or any of the biofuels blended at 30%. Other authors have observed the same tendency with rapeseed methyl ester [51]. In particular the SOF emissions are considerably higher for RME and in tests performed with cold start the ration SOF/PM is decreasing with increasing average speed.

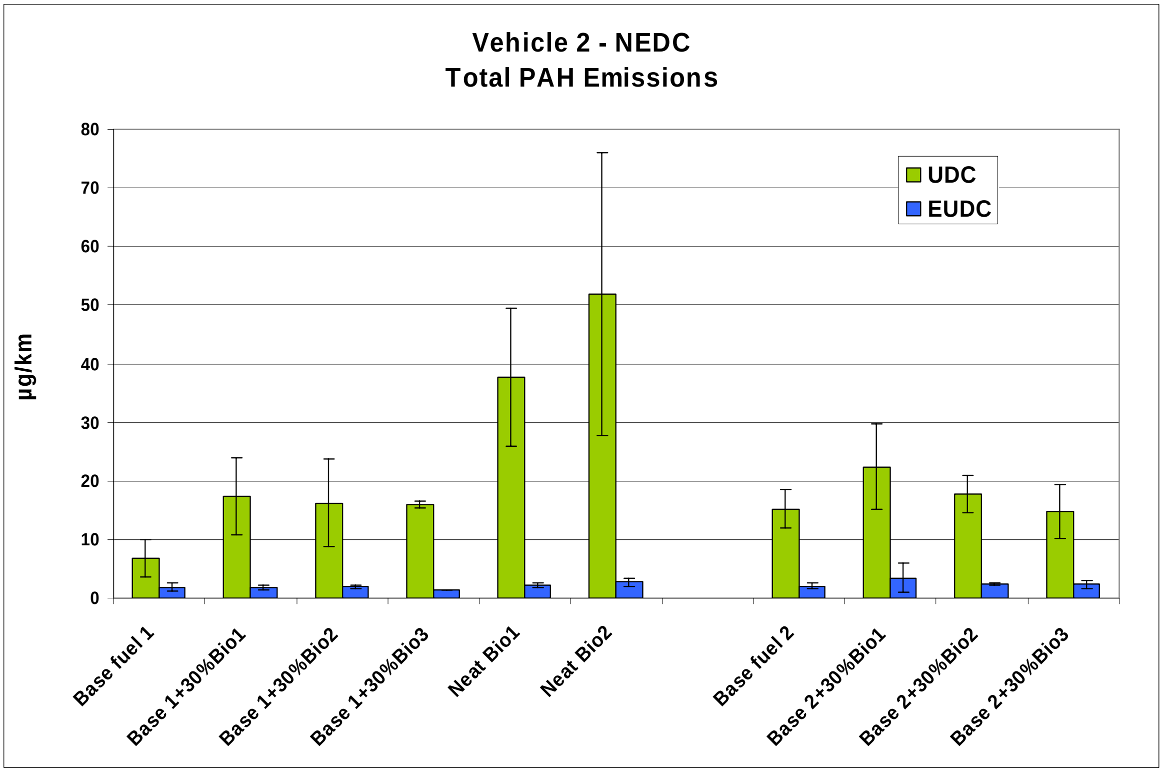
It should also be remarked when looking at the Fig. 58 that Reference fuel 1 is a very severe reference for biodiesel than the market average fuel quality and for this reason PAHs emissions coming out from Vehicle 1 and the Base Fuel 1 are extremely low. In previous tests with similar type of vehicle (EURO 3) we found that the reference fuel emitted around 10-12 μg/km of total PAH. That means that all the results for the UDC part of the cycle performed with biodiesel blended at 30 % are perfectly below the range of emissions of a standard reference diesel. We could say the same for the values found during UDC part of the tests when the vehicle is fueled with neat biodiesel (7.1 and 5.0 μg/km). To confirm this point we will show later results for another reference fuel (designated as Base fuel 2) which will be more in accordance with an average fuel in the market.

Another fact which requires attention is the value corresponding to UDC phase performed with the Reference fuel 1 plus 30% of rapeseed methyl ester, which is much higher than the others. We have to remark that this result is extremely unreliable since the variation with 95% confidence interval is very high (47%) so that makes the result unacceptable. It could be possible that the addition of 30%

of biodiesel, by increasing the density of the new fuel, should also increase the emissions by decreasing the efficiency of the combustion. Nevertheless, it is hard to believe that the influence should be so large.

On the view on these results and *since the positive or negative effect on PM emissions varied significantly among vehicles, fuel and load* we decided to study what would happen if we should test the same fuels on a different car. In the following pages we will show results corresponding to the same tests performed with a different car but same fuel (Fig. 60) that will support the idea that this result is not a fuel related problem. A second Base fuel (marked as Ref fuel 2) which has properties more in line with the market average, was also tested in the second vehicle.

Fig. 59 Total PAH emissions: vehicle 2



A very quick look to the results for the second vehicle tested, which corresponds to a Unit injection system, showed that it has higher emissions than the vehicle 1 (common rail technology) when running with the same Base fuel 1. This information comes to corroborate the importance of the efficiency of the combustion process on the PAHs emissions.

We have to remark that all results during the EUDC are extremely good. The concentrations of PAHs measured during this phase of the cycle varied from 1,4 µg/km for Reference fuel 1 plus 30% of palm biodesel to 3,7 µg/km corresponding to Reference fuel 2 plus 30% of Biodiesel rapeseed. These results come to corroborate the good behavior that we already observed for the vehicle 1 during the EUDC.

The tests performed with vehicle 2 showed that Reference fuel 2 behaves worse than Reference fuel 1 during the UDC phase of the cycle. The results for the blended fuels, either with Reference fuel 1 or 2, are very similar. This fact comes to confirm that the base fuel 1 has very severe standard as explained when discussing regulated results (4.1.3. Gaseous and Particulate Emissions-Base fuel 2). No significant difference was observed for the this vehicle and fuel in the emissions coming from the EUDC phase (Values from 1,8 µg/km to 2,0 µg/km).

Both Neat biodiesel fuels showed, during the UDC phase, a very high variation with 95% of confidence (31 and 46 % respectively) which makes results objectionable. Even though, we have to consider the tendency of these two neat fuels to be higher emitters. Also the result coming out for UDC with Reference fuel 2 plus 30 % Biodiesel 1 can be objected since it shows a 32% of variation with 95% of confidence.

Results for vehicle 2, during UDC phase, using Base fuel 2 are very close to those of 30% Soya which is slightly higher (16%). The best result during this first part of the cycle corresponds to the blend of Reference fuel 2 plus 30% Biodiesel 3, which is slightly better since emits around 4% less that Reference fuel 2.

This demonstrates that Reference fuel 2 is closer to the behavior of a standard fuel and the emissions for the biodiesel mixtures either with fuel 1 or fuel 2 are also very low if we talk in absolute terms, always below the emissions of a standard EURO 3 vehicle with any other commercial fuel.

Fig. 60 Individual PAH compounds quantified in PM for vehicle 1

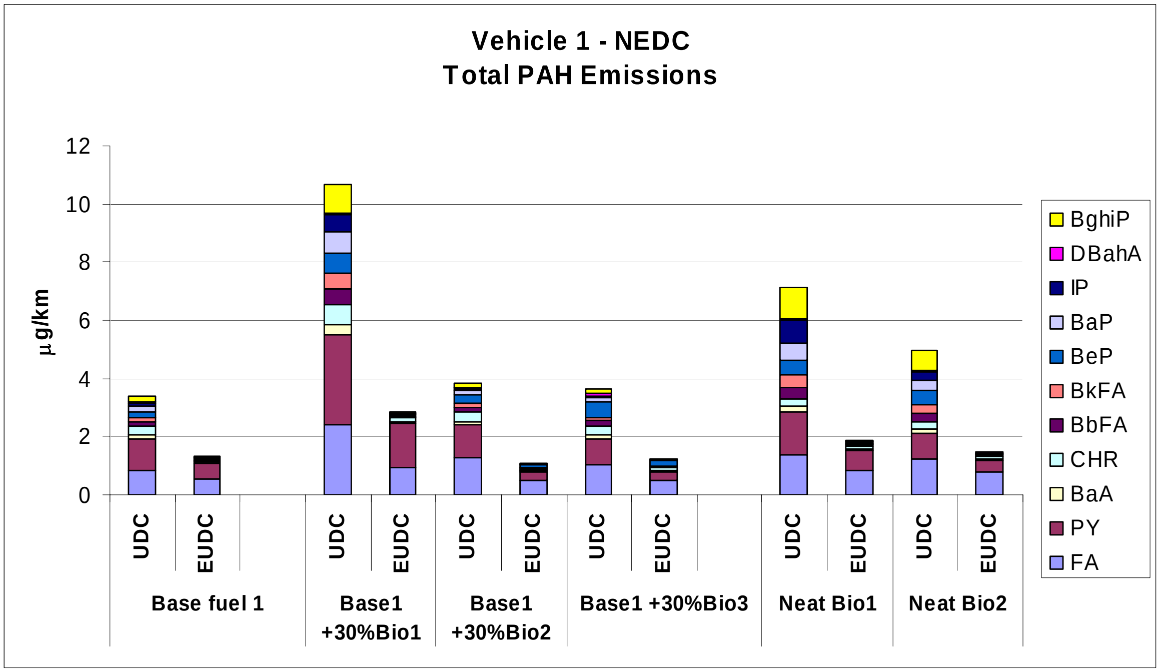


Figure 60 shows the results on the individual PAH compounds quantified in the PM collected for Vehicle 1. PAHs composition may give us very valuable information about the quality of the PM.

Looking at the distribution of these compounds we can find clear evidences of the differences between the quality of the PM emitted during the UDC and the EUDC.

As we have remarked before, the PM emitted during the first part of the cycle has a higher content of PAH due to the cold start. We can also say now that the emissions during UDC are also richer in content of big PAH with more than 4 rings. It is very possible that the different properties of the biodiesel affect in a larger extend the combustion process in these conditions more than when the engine is already warm. This situation leads to the fact that UDC emissions have very similar fingerprint during UDC phases for all fuels included the reference fuel

The percentage of the group including five and six rings, which are themselves responsible for most of the toxicity of this group, is very high for the two neat biodiesel (54% for neat biodiesel 1 and 50% for neat biodiesel 2 versus 32 % of the Reference Fuel 1). When biofuels are mixed at 30% with the reference fuel, the properties of the resulting fuel are not so different so the percentage of PAHs with 5 or 6 rings emitted is closer to the reference fuel 1 (39%, 26% and 34% respectively when 30% of Biofuel 1, 2 or 3 are mixed with the reference fuel 1).

Fig. 61.- Individual PAH compounds quantified in PM for vehicle 2

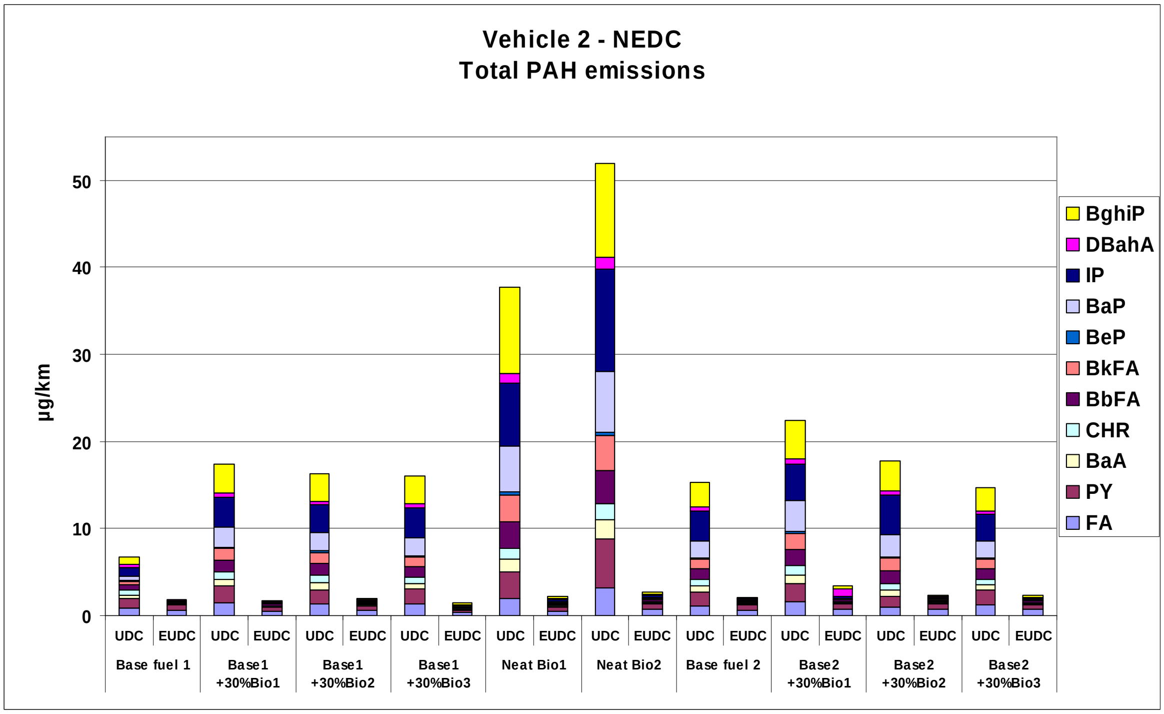


Figure 61 shows the results on the individual PAH compounds quantified in the PM collected for Vehicle 2. Here we can see that the differences between UDC and EUDC are even more evident. Both neat biodisel fuels showed a much higher amount of Benzo(g,h,i)perilene and indene(1,2,3-c,d)pyrene during the UDC phase.

All blended biodiesels at 30% have the same level of emissions and almost identical fingerprint. Neat biodiesels showed higher amount of PAHs but in all cases, they had shown the same profile. For both neat biodiesel 1 and 2 we have also seen higher amount of 5 and 6 rings (79% and 75% respectively for Neat biodiesel 1 and 2 *vs*. 57% of reference fuel) while the fingerprint do not differ too much from the blended fuels.

The results obtained with the biodiesel fuels in vehicle 2 during the second phase of the cycle, EUDC, were always at very low level and very close to emissions of reference fuel during. These emissions were also in very good agreement with the EUDC levels of emissions showed by the first car with common rail technology. Values for emissions during the EUDC, for vehicle 1 varied from 1,4 to 2,7 µg/km and for vehicle 2 from 2,1 to 3,5 µg/km .

4.4.4. Azaarenes concentration in the particulate exhaust of LD vehicles fuelled with biodiesel

Content of Azaarenes (Aza-PAH) in PM may give us some extra information but they will not add too much new to what we already known from the PAH results. Moreover, we are talking about very small values which are at their highest 1,2 µg/km and they do not represent more 0,00003% of the total PM. We have anyway considered the analysis of these compounds since they posses a higher solubility and mobility in the environment than PAHs and they are also potential mutagenic and/or carcinogenic [57]

Fig. 62.- Total Aza-PAH emissions: vehicle 1

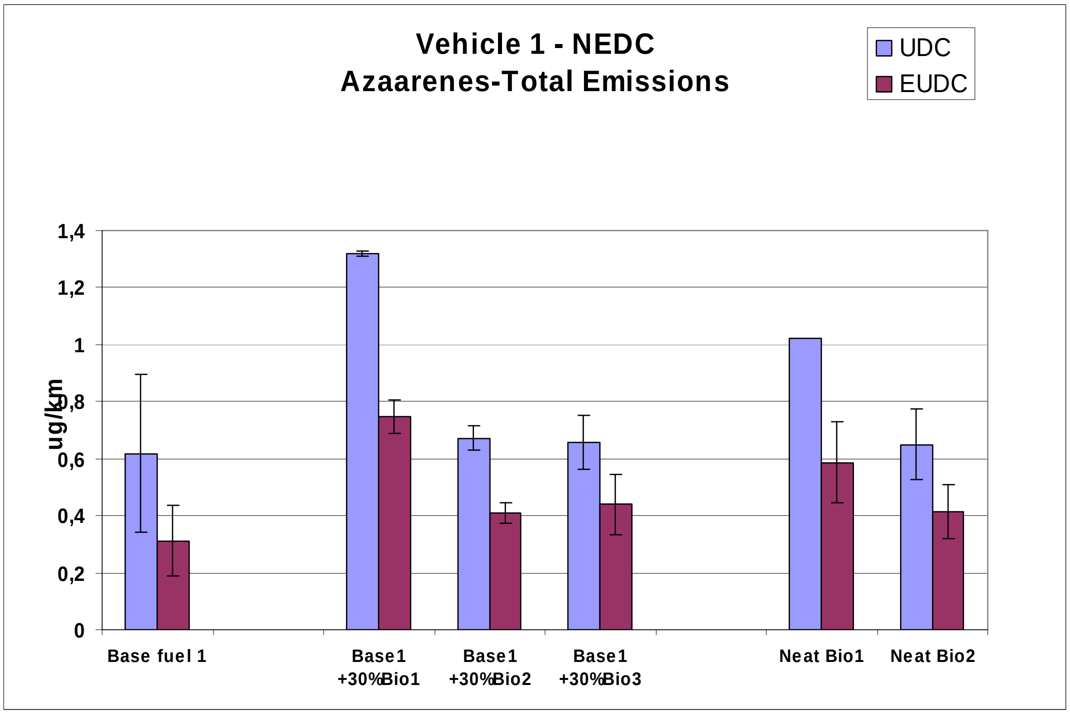


Figure 62 is showing the variation of Aza-PAH emissions (µg PAH/km) of the exhaust obtained for the 1st vehicle running the European Driving Cycle.

The first important thing to notice in figure 62 is that aza-PAH have the same trend as PAHs. Once more, we observed that during UDC the values of aza-PAHs emitted by all fuels tested are higher than during the EUDC. The only difference is that in this case the variation between the to cycles is not as big as it was for PAHs.

The blend fuel containing a 30% of Biodiesel 1 in the base fuel 1 is, once more, the highest emitter.

Fig 63.- Individual Aza-PAH compounds quantified in PM for: vehicle 1

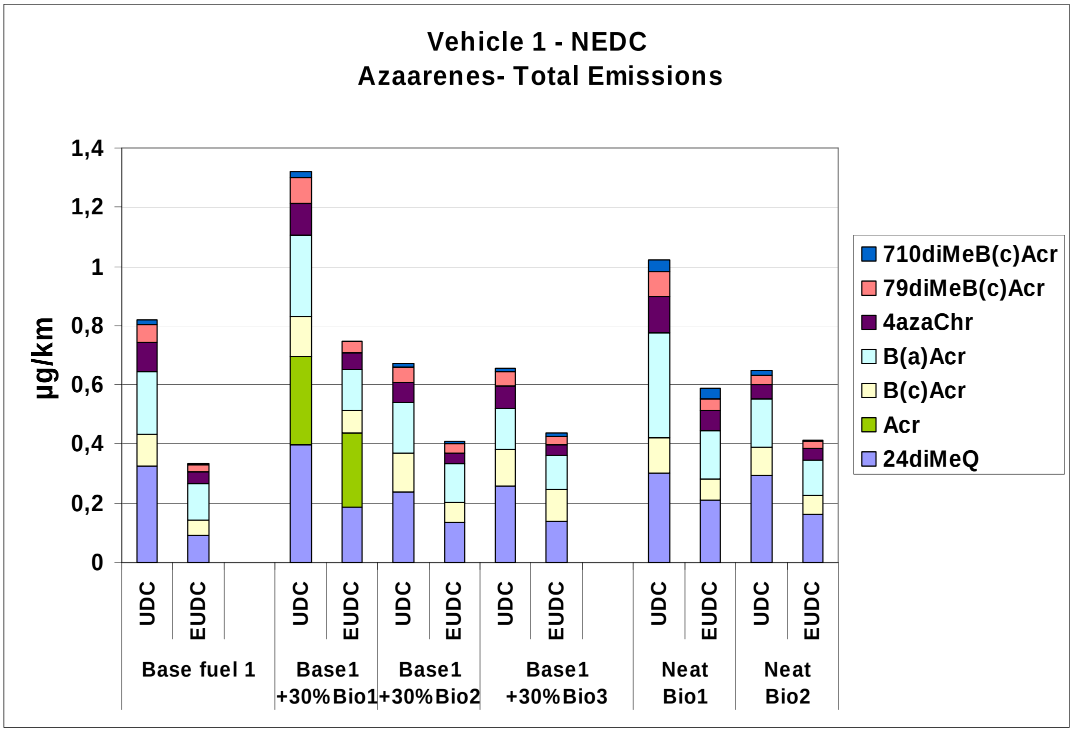


Figure 63 shows the results on the aza-PAH compounds quantified in the PM collected for Vehicle 1. If we keep apart the situation for Reference fuel 1 plus 30% of Rapeseed methyl ester which has higher emissions and includes acridine, all the other fuels showed a very similar profile, even between the two phases of the cycle. Nor really significant differences between the composition and fingerprint of emissions from UDC or EUDC.

Fig. 64.- Total Azaarene emissions: vehicle 2

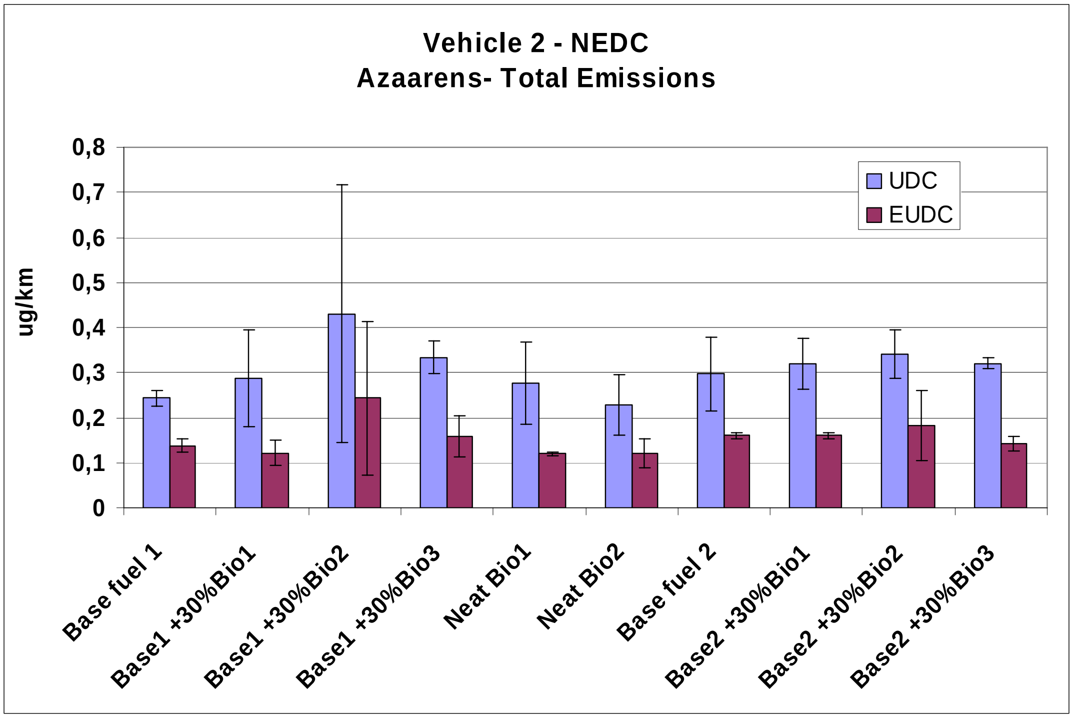


Figure 64 shows the variation of aza-PAH emissions (µg PAH/km) of the exhaust obtained for the 2nd vehicle running the European Driving Cycle. For this vehicle the results are more uniform than for 1st vehicle. The level of emissions between the UDC and the EUDC are not as different as they were for the PAH and not big differences were observed between the two reference fuels either. The only fact susceptible for a comment is that this is the only time in which the vehicle 2 produces an amount of a type of pollutants in the exhaust lower that the vehicle one.

We should remark that the values for the test performed for the Reference fuel 1 + 30% of biodiesel 2 should excluded due to the high uncertainty (no statistical significance at 95% confidence level).

Fig. 65.- **Individual Aza-PAH compounds quantified in PM for: vehicle 2**

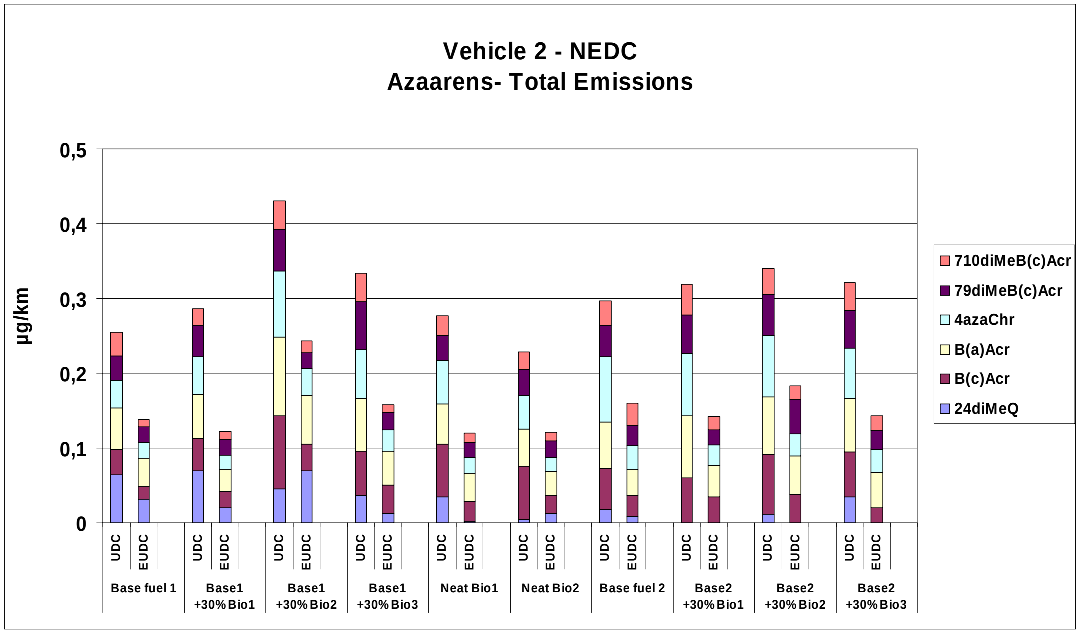


Figure 65 shows the results on the aza-PAH compounds quantified in the PM collected for Vehicle 2. The profile is very similar to what we already saw for vehicle 1. Fingerprint for UDC and EUDC part of the cycle are almost the same.

4.4.5. Overall potential toxicity of the Mixture: Particulate toxicity from polycyclic aromatic compounds

The measurement of the total mass and the size distribution of the particulate is not always enough to evaluate its toxicity and carcinogenicity, so the chemical composition analysis of particulate appears important to contribute to a more complete assessment of the impact on human health.

The mechanisms determining the presence of PAHs in the exhaust gases and adsorbed on particulate are complex and varied. We can list the following:

- PAHs already present in the fuel that escape the process of combustion.
- PAHs formation from non PAHs compounds.
- Modification of PAHs contained within the fuel.
- PAHs absorbed by the lube oil from the fuel and then released, plus a small amount already present in the lube oil.

In order to evaluate the potential toxicity and carcinogenicity of these pollutants the method based on the benzo(a)pyrene Toxicity Equivalency (TEQ) approach has been used [25]. By means of this approach, to each individual PAH is assigned a toxicity factor (TEF) relative to benzo(a)pyrene, B(a)P, that is set to unity. The B(a)P toxicity equivalent (TEQ) of a given sample is calculated as the sum of each PAH concentration (Ci) multiplied by their TEF over all the measured compounds:

$$\mathbf{TEQ = \Sigma\,[\,Ci] \times TEF\ i}$$

(TEF = “Toxicity Equivalence factor” e TEQ = “Toxicity Equivalence”)

We have applied this approach to the PAHs results showed previously for the two LD vehicles.

Fig 66.- Toxicity equivalent for emissions from Vehicle 1

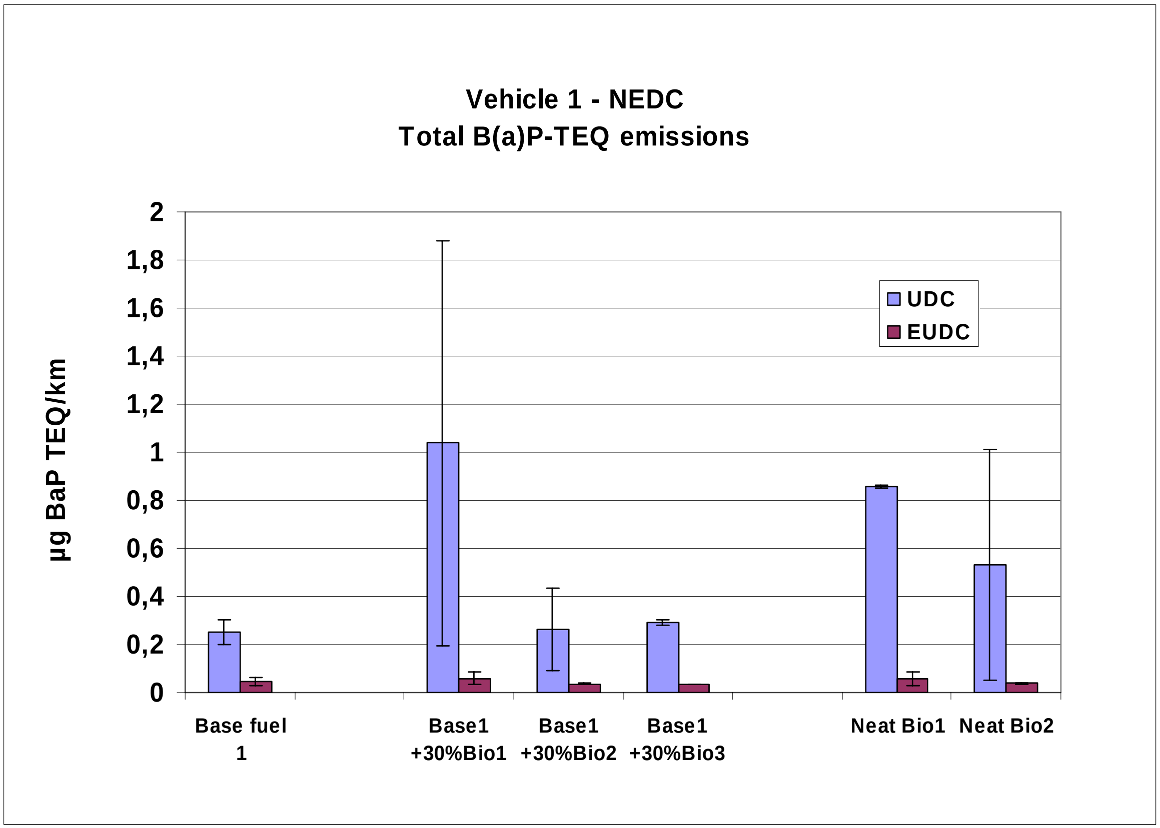


Figure 66 shows a profile for the overall potential toxicity of the Mixture, which is the logical consequence of the concentrations already reported for total PAH**.** We can observe that the TEQ values coming out during the first part of the driving cycle (UDC) when using neat biodiesel, are higher than the one obtained with the reference fuel. Only the fuel prepared from reference fuel plus 30% of Palm oil methyl ester has a very similar result during UDC if compared to Base fuel 1. On the opposite, the toxicity during the EUDC phase is very low for all the tests performed with biodiesel, either neat or blended, and always in the same range of the Reference fuel 1.

We have to exclude the results of the UDC phase for Base fuel 1 plus 30% of biodiesel 1 and 2, as well as for neat Biodiesel 2, due to the uncertainty of these two results. For some reason, the combustion coming to these results have given such different results that the chemical compositions of the two repetitions are too different to be considered. This has already been noticed when discussing the results for the total amount of PAHs for Vehicle 1 and 2 and now, when calculating the Toxicity equivalent of these mixtures, the uncertainty is even higher since the compounds with more variation are those with higher TEQ value.

Fig 67.- Toxicity equivalent for emissions from Vehicle 1

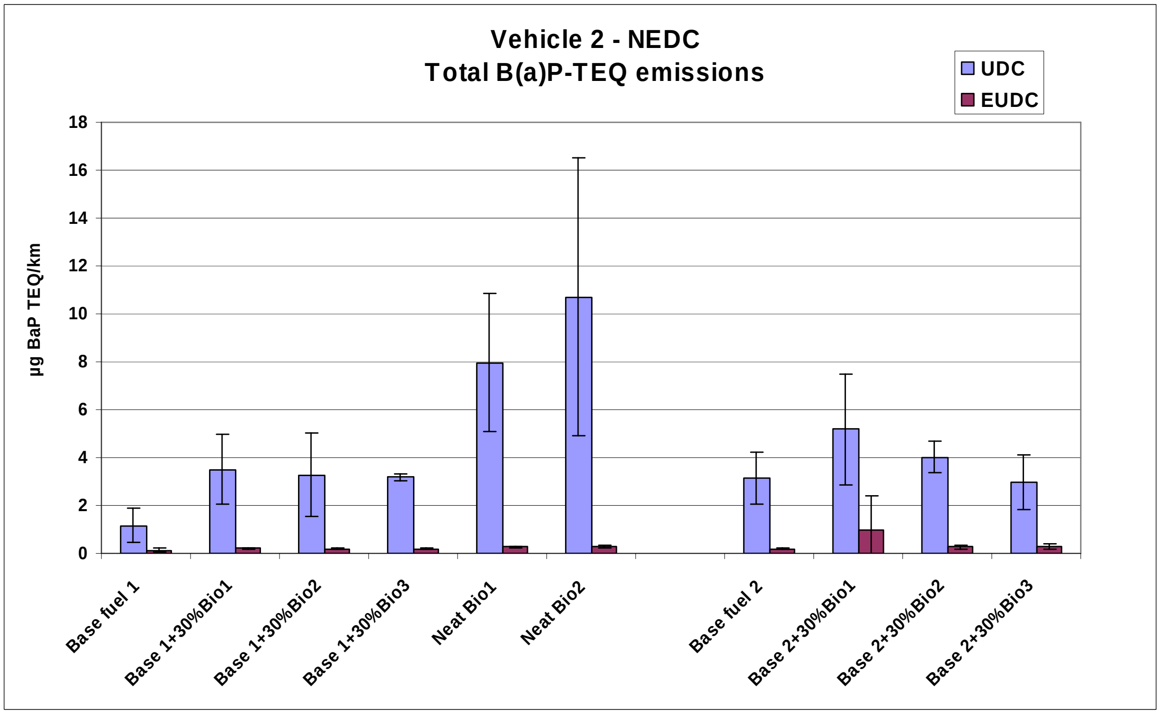


Figure 67 shows the values of potential toxicity of the mixture of PAHs for Vehicle 2. Once more, we can see the clear tendency the toxicity to increase during the UDC phase of the cycle when increasing the amount of Biodiesel. For the Reference fuel 2 the differences with the blended fuels are smaller. Once again we have to exclude of consideration some results due to the high uncertainty. In particular the results for Neat biodiesel 1 and 2 are very unreliable. The same can be said for: Base fuel 1 plus 30% of biodiesel 1 and 2 (UDC phase), Base fuel 2 plus 30% biodiesel 1 (UDC and EUDC), Base fuel 2 plus 30% biodiesel 3 (UDC).

4.4.6 . Gaseous emissions: Volatile Organic Compounds

Ozone, as well as particulate matter (PM), is a major problem with respect to human health effects and the vegetation. It is a toxic gas, constituted by unstable molecules that easily split to release molecular oxygen (O_2) and an extremely reactive oxygen atom (O_3 —> O_2+O). Thus it's a strong oxidant and it represents one of the principal factors determining photochemical smog.

Since ground-level ozone is one of the air pollutants of most concern in Europe, a current subject is the determination of the C_2-C_9 ozone precursor hydrocarbons (2D–GC with dual FID detection), both with respect to characterizing emission sources and to monitoring ambient air quality. The new Ozone Directive 2002/3/EC, which has been in force in September 2003, obliges member states in the future not only to monitor ozone itself but also its photo-chemically reactive precursors in the air, namely nitrogen oxides and 31 Volatile Organic Compounds (Table 1).

Table 1. The 31 ozone precursors VOCs recommended for measurements in the Ozone Directive 2002/3/EC.

Ethane	trans-2-Butene	n-Hexane	m+p-Xylene
Ethene	cis-2-Butene	i-Hexane	o-Xylene
Ethyne	1,3-Butadiene	n-Heptane	1,2,4-Trimethylbenzene
Propane	n-Pentane	n-Octane	1,2,3-Trimethylbenzene
Propene	i-Pentane	i-Octane	1,3,5-Trimethylbenzene
n-Butane	1-Pentene	Benzene	
i-Butane	2-Pentene	Toluene	Formaldehyde
1-Butene	Isoprene	Ethylbenzene	NMHC

One of the major objectives of this directive is to assist in the attribution of emission sources to pollution concentrations. Each VOC reacts in the air at a different rate and with different reaction mechanisms and thus, VOCs can differ significantly in their influence on ozone formation. A sensitive and selective analytical technique, reliable also in-the-field is essential for source apportionment. The use of cryogen-free gas chromatographs facilitates real-time air monitoring at remote locations [7] for short periods of time and on a continual basis, throughout the year [8, 9] in urban areas. In the latter case, the most important contributor to ozone precursors is road traffic [10], thus the investigation of ozone precursor VOCs in vehicle emissions is of great concern

4.4.7. Speciation of Volatile Organic Compounds (VOCs)

Volatile organic compounds (VOCs) are a fraction of the total hydrocarbons emitted into the air from vehicle exhausts. These emissions undergo chemical reactions in the atmosphere, which cause a number of indirect effects, in particular the formation of photochemical oxidants such as tropospheric ozone ("photochemical smog") and greenhouse gases. Moreover, among VOCs, benzene and 1,3-butadiene have harmful effects on health.

The reactions involved in these processes are:

$NO_2 + h\nu \rightarrow NO + O \quad (295\ nm < \lambda < 430\ nm)$

Where the nitrogen dioxide absorbs UV-VIS light that penetrates into the troposphere: at a wave length inferior to 430 nm the radiation absorbtion induces photodissociation.

The successive reaction between atomic oxygen, molecular oxygen and a species (M) capable of absorbing the excess energy that forms (in general molecular nitrogen), is the principal source of ozone in urban atmosphere:

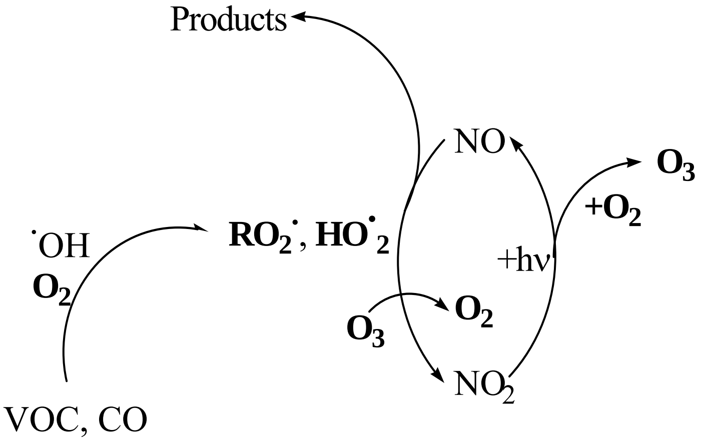
$$O + O_2 + M \rightarrow O_3 + M$$

The rapid reaction between NO and O_3 completes this cycle of reactions, known as the NO_2 photolitic cycle:

$$NO + O_3 \rightarrow NO_2 + O_2$$

Nevertheless, the presence of hydrocarbons and other organic compounds in the atmosphere determines the breaking of the cycle, through competitive reactions that convert NO to NO_2 without ozone consumption, and that are responsible for the accumulation of ozone in the troposphere associated with photochemical smog. The entire reaction cycle is represented in figure 68. This NO subtraction by $RO_2\cdot$ is at the base of ozone ground level accumulation.

Fig 68- Radical reaction scheme of ozone formation starting from VOC



Oxidation of non-methane hydrocarbons, emitted from traffic, leads to the formation of peroxyradicals [$RO_2\cdot$], which react with the nitrogen monoxide breaking the photolitic cycle of NO2:

$$OH^\bullet + RH \rightarrow H_2O + R^\bullet$$

$$R^\bullet + O_2 \rightarrow RO_2^\bullet$$

$$RO_2^\bullet + NO \rightarrow RO^\bullet + NO_2$$

4.4.8. Ozone formation: evaluation method

For the present study we have performed vehicle emission measurements of 30 individual C_2-C_9 hydrocarbons specified in the Ozone Directive and we have calculated the potential impact of the identified and quantified sources on ozone formation through the Maximum Incremental Reactivity (MIR) approach, developed by W.P.L. Carter and used in "Low emission vehicles and clean fuels" regulations in California [11]. The MIR is the ozone variation, caused by adding a small amount of test VOC to the emission in a photochemical smog episode, divided by the amount of test VOC added. It can be used to assess the impact of changing emissions of an individual VOC on ozone formation:

$$\mathbf{MIRi = max \{ d[O_3]p / dEi \}}$$

Where $[O_3]p$ is the peak ozone formation and “Ei” is the emission of the VOCi

Knowing the MIR values we can use them to calculate the Potential ozone (PO_3(g/km)) formation of an exhaust emission by using the following equation:

$$\mathbf{PO_3(g/km) = \Sigma i\{MIRi\ (g\ O_3/g\ VOC)\ Ei(g/km)\}}$$

Once we have measured the concentration of each VOC emitted (ppm), we calculate the mass (as g/km) and then we calculate the sum of the product of every VOC mass by their corresponding MIR factor. The result corresponds to the quantity of ozone that could potentially be formed.

To carry out this part of the study passengers cars were driven on a chassis dynamometer (Zoellner GmbH) with a constant volume sampler (flow 7.5 m^3/min). Ten liters of vehicles exhaust samples were collected in Tedlar™ bags and successively connected to the analyzer inlet. Only a limited sample volume of 80 ml was collected and analyzed for each driving test allowing replicated analysis if necessary.

A thermal desorption unit (UNITY™) and an auxiliary sampling device (Air Server™) from Markes International (Pontyclun, UK) were used to collect samples from ambient air or Tedlar bags of exhaust gases. Analysis were performed with a gas chromatograph (6890, Agilent, Wilmington, DE, USA) equipped with dual flame ionisation detector (FID). [12]

In order to investigate the contribution from different fuels with content on biodisel to the 30 ozone precursors hydrocarbons in the air we conducted a number of emission measurements from the same LD vehicle 1 considered before.

4.4.9. Volatile organic Compounds and their contribution to the Ozone formation: Experimental results

Considering the values for the total hydrocarbons (HC) showed in this report when talking about regulated emissions, we may expect also a similar behavior in the sum of VOCs (sum of the C_2-C_9 ozone precursor hydrocarbons included in the Ozone Directive 2002/3/EC).

Fig. 69.- Variation of total emissions of Volatile Organic Compounds: Vehicle 1

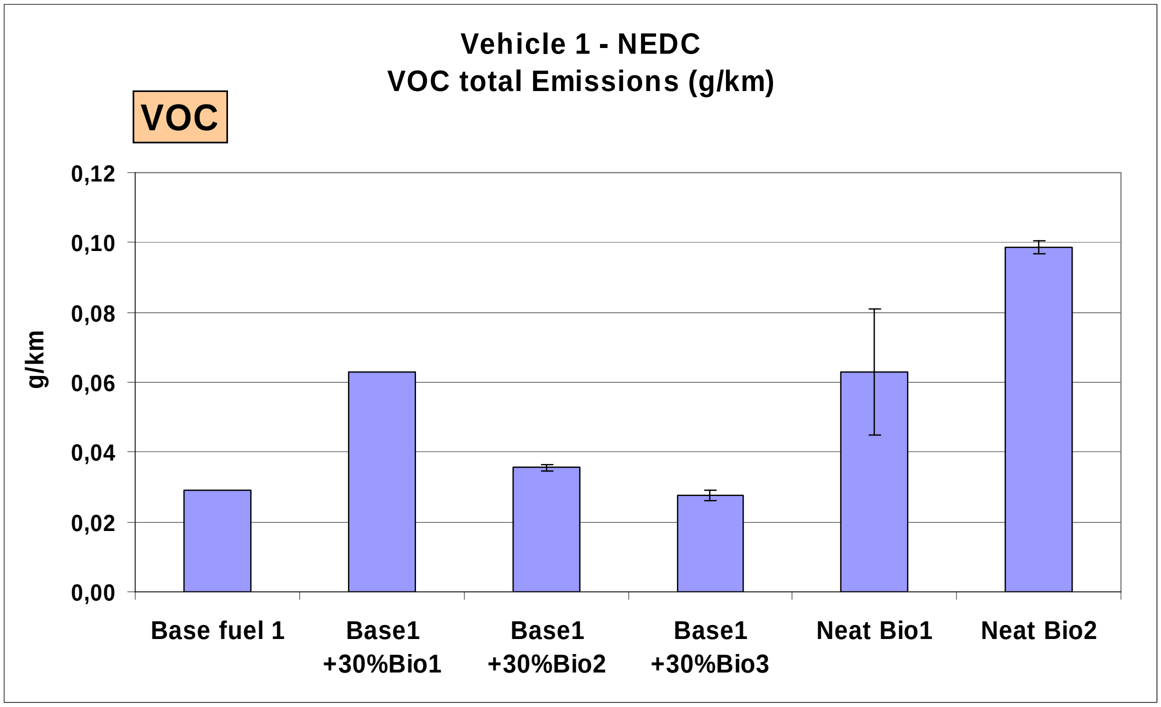


Figure 69 shows the values for the sum of the C_2-C_9 ozone precursor hydrocarbons included in the Ozone Directive 2002/3/EC. For the first two tests only one sample could be taken. For the other experiments, the repeatability was very good excluding the results for the neat biodiesel 1.

The total amount of volatile hydrocarbons which have been quantified this way follow the same trend of the total non methane HC measured in previous pages (see Figure 5). When quantified separately we can observe that the amount of VOCs present in the exhaust coming from Biodiesel is, in most cases, slightly higher if compared to the reference fuel in all LD vehicles considered in this study.

The amount of unburned VOCs emitted from this particular car increased by a factor 2,1 when 30% of rapeseed methyl ester is added to the reference fuel, indicating the that the different properties of this biodiesel blend can make the engine to operate in unsuitable conditions. Neat biodiesel 1 increases the emissions in a very similar way while neat biodiesel 2 increase is even higher (factor 3.3) if compared to reference fuel.

Emissions found for Biodiesel 2 blended at 30% is only 20 % higher than reference fuel while Bio 3 blended at 30% was the only one which demonstrated to be slightly better than reference fuel (7% lower emissions.)

In order to study the contribution from these ozone precursor hydrocarbons we have the relative contribution of each individual VOC to the potential ozone formation, estimated by the Maximum Incremental Reactivity (MIR) Approach which has been calculated as described before (4.4.8). The pattern observed is the same as the one showed in the figure 69 for VOCs and so the fuels with higher potential for the ozone formation are the two biodiesel.

Fig. 70.- Variation of total emissions of Ozone Potential Formation for Vehicle 1

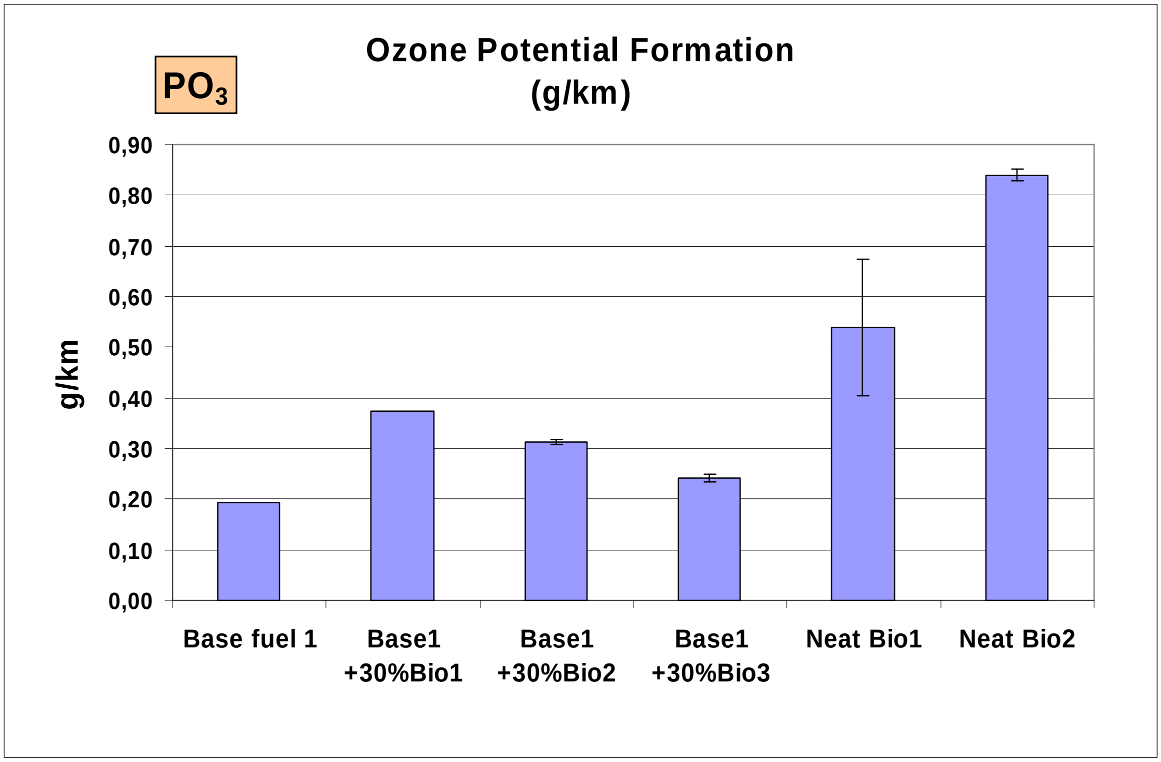


Figure 70 shows to the quantity of ozone that, potentially, could be formed considering the concentration of each VOC emitted (g/km) when we calculate the sum of the product of every VOC mass by their corresponding MIR factor.

We can observe that the potential to generate ozone from these volatiles compounds increases when increasing the amount of Biodiesel. For blends created from 30% of Biodiesel 2 or Biodiesel 3 with the reference fuel the differences for emissions are very small (30% of Bio 2 emits 1,6 times more and 30% Biodiesel 3 emits 1,2 times more than reference fuel). Once again we have to question the result for the Neat Biodiesel 1 due to the high uncertainty.

5. Conclusions

Based on the results of this study, and despite all limitations of the project plan and scope, the following conclusions can be drawn:

1. In general, it can be said that the use of biodiesel may lead either to a reduction or to an increase of the emissions depending on:
    - The pollutant considered
    - The diesel fuels used to establish the emission base line
    - Content of biodiesel in the fuel
    - Vehicle technology and engine settings
    - Engine operating conditions
    - Driving cycle and driving cycle phase

    The magnitude of emission variations due to the use of biodiesel often resulted to be in the same range of the variations noticed comparing two different diesel fuels.

2. This study confirms that the higher the biodiesel content the higher the influence on emissions. The most substantial effect is observed when neat biodiesel is used; the results obtained suggest that the very different properties (density, distillation curve, heating value, and viscosity) of biodiesel compared to a standard diesel fuel can make the engine operate in non optimum conditions and, as a consequence, certain pollutants may increase significantly.

3. The effect of biodiesel on regulated pollutant can be summarized as follows:
    - In comparison with the Base Fuel 1, all the fuels containing biodiesel led to an increase of CO and HC emissions for both vehicles tested; this increase was very low in the case of the blend containing 30% of biodiesel from palm oil. Neat biodiesels increased HC and CO emissions to a much larger extent than the 30% blends. When a different base diesel fuel was used (Base Fuel 2), the effect of biodiesel on HC and CO emissions was largely reduced. The increase of CO and HC emission resulted to be concentrated in the very first phase of the driving cycle while, especially over the extra-urban part of the cycle, no difference or even a decrease was noticed.
    - In general, NOx emissions were marginally affected by the presence of biodiesel in the fuel. Only with neat biodiesel a slight but statistically significant increase was noticed.
    - In general the total particulates mass measured over the NEDC cycle was reduced by biodiesel in both the test vehicles. However the magnitude of reduction resulted to be dependent on the vehicle (it was much larger for Vehicle 1 than for Vehicle 2) and on the phase of the cycle considered. In most cases the reduction of PM emissions measured over the extra-urban part of the cycle was much larger than over the urban part; in the case of Vehicle 2 fuelled with neat biodiesel, particulates emissions even increased over the urban phase.

4. The results have put in evidence that the cold start is the most critical phase of the cycle for the fuels containing biodiesel; the HC and CO emission variations due to biodiesel in comparison with the base fuels were concentrated in the first 200-300 s of the driving cycle.

5. The analysis of particulates composition (performed only for vehicle 2) showed that while soot emissions were always reduced with fuel containing biodiesel, the SOF fraction considerably increased especially when neat biodiesel was used. This effect has been widely reported in the literature and mainly occurs at low loads and speeds. This can explain the very different effect of biodiesel on particulate emissions noticed over the two parts of the cycle: it seems that in the urban phase the reduction of soot was partly or totally counterbalanced by the increase of the SOF fraction. As SOF fraction typically consists of heavy unburned hydrocarbon adsorbed on the soot particles, its increase is consistent with the higher HC and PAHs emissions measured over the urban part of the cycle.

6. The mass/size distribution of particulates emissions measured with a Low Pressure Impactor showed that, for Vehicle 1, the fuels containing biodiesel reduced the mass in all the size bins. In the case of Vehicle 2, the mass associated with fine particles was reduced while increased for the larger particles. Nevertheless the total mass was reduced in all the cases.

7. The two test vehicles exhibited a different response, in terms of magnitude and direction of emission variations, to the fuels containing biodiesel. From this programme it is not possible to conclude what is the parameter responsible of this different response; some results seem to suggest that the engine settings of the two vehicles were different and this could explain, at least partly, the different behaviour. However, also the different injection technology could have played an important role.

8. The origin of biodiesel or, in other words, the vegetable oil used to produce the biodiesel, seems to have a very limited effect on emissions. Only in the case of palm oil, its higher cetane number have some positive effects on CO, HC and PAHs.

9. The type of engine and its setting has a great influence on the results of Polyaromatic compounds in the PM**.** The use of either neat biodiesel or blended mixtures at 30% in light duty passenger cars has not a visible positive influence in the quality of the emissions in terms of toxicity during the first part of the cycle

10. PAHs content of the PM, and so their potential toxicity, may increase during the UDC part of the cycle with biodiesel, either neat or blended at 30% in both vehicle 1 and in vehicle 2. This behaviour was not ever observed in the emissions from the same vehicles during the EUDC where all biodiesel, pure or blended, showed results on the same range as reference fuels and sometimes, even lower. The lowest PAH emission was obtained for fuel containing 30% of Palm biodiesel.

11. During the whole test programme the use of biodiesel showed a very similar range of variation if we compare it with previous programmes in which different qualities of standard diesel fuel were tested. Even more, biodiesel emissions never went over the values obtained for other EURO 3 LD vehicles tested previously in our laboratories.

12. Individual PAH composition did not show a significant variation when using different mixtures of reference fuel plus any type of biodiesel. Only when neat biodiesel was used the amount of 5 and 6 rings increased during the UDC phase while fingerprints remained the same.

13. Variation of VOCs followed the same pattern as the HC measured with the regulated emissions. VOCs emissions from biodiesel increased by a factor 1,2 to 3.3 referred to the reference fuel. The lowest VOCs emission corresponds to the fuel blended with 30% of Palm oil methyl ester.

14. The use of 30% of palm biodiesel blended with reference fuel showed a noticeable improvement in the quality of non-regulated emissions. Among the different mixtures prepared, this biodiesel blend is the one that had a slightly better behaviour in terms of PAH and so for TEQ. Also the results for VOC and their corresponding ozone potential formation were found to be better.

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European Commission

EUR 22745 EN– DG Joint Research Centre, Institute for Environment and Sustainability

Title: Effect of Biodiesel Fuels on Pollutant Emissions from EURO 3 LD Diesel Vehicles (1)
Authors: G. Martini, C. Astorga, A. Farfaletti, M. Botta, M. Rey, U. Manfredi, A. Krasenbrink, B. R. Larsen and G. De Santi
Luxembourg: Office for Official Publications of the European Communities
2007 - 94 pp. – 21 x 29.7 cm
EUR - Scientific and Technical Research series; ISSN 1018-5593
ISBN 978-92-79-05536-2
Luxembourg: Office for Official Publications of the European Communities

Abstract:

Transport is a key factor in modern economies. However, the EU transport system is currently not sustainable, and in many respects moving away from sustainability rather than towards it. The European Environment Agency highlights in particular the sector's growing CO2 emissions that threaten the EU meeting its target under the Kyoto protocol. Transport also represents a key challenge to sustainability in terms of depletion of resources and European competitiveness, safety and security concerns, especially due to the monolithic reliance on a single energy source.

As stated in the Commission’s November 2000 Green Paper on security of supply, in 1998 energy consumption in the transport sector was to blame for 28 % of emissions of CO2, the leading greenhouse gas. In particular, road transport alone accounts for 84 % of the CO2 emissions attributable to transport.

Furthermore, in terms of security of energy supply, there is growing concern for the current situation of transport sector that depends on crude oil for more than 99%.

In the above mentioned Green Paper the European Commission has also identified the measures to tackle these problems and, among them, one the most important is the promotion of alternative fuels; the ambitious target that has been proposed by the Commission is to replace 20% of conventional fuels with substitute fuels by 2020.

According to the Commission White Paper “European transport policy for 2010: time to decide” the most promising forms are biofuels in the short and medium term, natural gas in the medium and long term and hydrogen in the very long term.

On the basis of the above mentioned Papers, in 2003 the European Union has adopted two Directives, the EC/2003/30 and the EC/2003/96, with the overall objective of promoting the use of biofuels. The first Directive set the targets for market share of biofuels for 2005 (2% in terms of energy content) and 2010 (5.75%); the second Directive set the framework for tax incentives for the promotion of biofuels.

Biodiesel is currently the most produced biofuel in Europe: the production in 2003 was about of 1500000 (EU25) tons with an increase of more than 32% compared to the 2002 figure.

Within this policy framework, the Joint Research Centre and the European Biodiesel Board have decided to cooperate to investigate the effect of biodiesel on pollutant emissions from diesel engines. In particular, in this report the effect of biodiesel fuels produced from different raw materials on the regulated emissions from light duty diesel vehicles are compared to the effect on other regulated and unregulated pollutants.

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LB-NA-22745 EN C

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Publications Office
Publications.eu.int

ISBN 978-92-79-05536-2
9 789279 055362