

Effect of Reformulated Fuels on Pollutant Emissions from Vehicles Part 2: Diesel Fuel / Water Emulsions

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Luxembourg: Office for Official Publications of the European Communities, 2005

ISBN 92-894-9744-0

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Printed in Italy

PART 2

List of Special Terms and Abbreviations

ACN	Acetonitrile
APCI	Atmospheric pressure chemical ionisation
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

Particulate matter (PM) is one of today's most challenging environmental problems in urban environments. A number of studies have pointed to adverse health effects of particulate matter with a diameter below 10 μm (PM10). Limit values for PM mass concentrations in ambient air expressed as PM10 is frequently exceeded in major cities and WHO (World Health Organization) has worked out that in Europe more than 100.000 people suffer premature death every year from effects of air pollution with PM10 being of major importance. A recent major public health impact study of PM10 in 19 European cities on a population of 32 million inhabitants has estimated that reducing long term exposure to PM10 concentrations by only 5 $\mu\text{g}/\text{m}^3$ in these cities may prevent between 3300 and 7700 early deaths annually. What's more, a recent major epidemiological study in 23 North-American metropolitan areas has demonstrated that PM10 pollution even plays a role in post neonatal infant mortality such as the sudden death syndrome and respiratory diseases.

Exhaust from Heavy duty (HD) and light duty (LD) diesel vehicles is an important source of PM and even though emission standards have been designed to curb the pollution from these traffic sources, they are still counting as the major contributors to PM in urban environments. Epidemiological studies in eight major European cities conclude that cardiac admissions in is likely to be mainly attributable to diesel exhaust.

In the diesel sector, engine technology is in continuous development and a number of after-treatment systems have been found which in combination with an enhanced fuel quality reduce emissions of PM, such as the oxidative catalyst and the particle trap. Today, the oxidative catalyst is incorporated in all modern LD diesel vehicles, which meets the EURO-3 and equivalent standards. The particle trap is an expensive and complicated solution not yet common in diesel vehicles. Nevertheless, in order to meet future stricter emission standards the particle trap seems unavoidable for LD and could be one of the future options for HD vehicles. However, there is a notable time lag between the introduction of a new emission standard or a new engine technology and the renewal of the vehicle park and as a short term alternative to the particle trap new fuel formulations may be employed to abate particle emissions.

Together with particulate matter diesel exhaust (DE) contains a group of regulated constituents i.e. carbon monoxide (CO), hydrocarbons (HC), and nitrogen oxides (NO_x), and a number of compounds that are not specified by the emission standards. The analysis of such compounds as individual species in DE is important either due to their carcinogenic properties, which is the case for polynuclear aromatic hydrocarbons (PAHs), or due to their potential for photochemical ozone formation, such as the volatile organic compounds (VOC).

Under the framework of collaboration between Regione Lombardia, Italy and the European Union Joint Research Centre the effect of alternative, reformulated, and modified fuels on pollutant emissions from diesel vehicles are investigated by the Vehicle Emission Laboratory (VELA). In this report, the reductions in PM emissions from LD diesel engines obtained by using diesel fuel/water emulsions are compared to the effect on other regulated and unregulated pollutants.

Acknowledgement

This experimental programme has been carried out with the essential contribution of:
R. Colombo, G. Lanappe, M. Sculati, P. Le Lijour, I. Fumagalli, M. Carriero, A. Brunella.

EFFECT OF REFORMULATED FUELS ON POLLUTANT EMISSIONS FROM DIESEL VEHICLES

PART 2: DIESEL FUEL / WATER EMULSIONS

1 Summary / *Sommario e conclusioni*

Particulate matter (PM) is one of today's most challenging environmental problems in urban environments. A number of studies have pointed to adverse health effects of particulate matter with a diameter below 10 μm (PM10). Exhaust from heavy duty (HD) and light duty (LD) diesel vehicles is an important source of PM and even though emission standards have been designed to curb the pollution from these traffic sources, they are still counting as the major contributors to PM in urban environments.

In the diesel sector, engine technology is in continuous development and a number of after-treatment systems have been found which, in combination with an enhanced fuel quality, reduce emissions of PM, such as the oxidative catalyst and the particle trap. Today, the oxidative catalyst is incorporated in all modern LD diesel vehicles, which meets the EURO-3 and equivalent standards. The particle trap is an expensive and complicated solution not yet common in diesel vehicles. Nevertheless, in order to meet future stricter emission standards the particle trap seems unavoidable for LD and could be one of the future options for HD vehicles. However, there is a notable time lag between the introduction of a new emission standard or a new engine technology and the renewal of the vehicle park and as a short term alternative to the particle trap new fuel formulations may be employed to abate particle emissions. The emulsion of conventional diesel fuel and water, produced by addition of a small amount of water and an appropriate surfactant to the fuel, has recently gained popularity for HD diesel engines, especially in the public transport sector.

However, the spread of water/diesel emulsions has been sometimes followed by strong debates on the actual effectiveness of such products in reducing pollutant emissions from vehicles and on the advisability of promoting the emulsions by means of fiscal incentives. For such reason, the JRC and the Regione Lombardia, under the framework of a Memorandum of Understanding signed by these two organizations, have decided to perform a joint study on this subject. In particular, an experimental programme has been carried to investigate the effect of diesel fuel/water emulsions on pollutant emissions from diesel vehicles. In this report the main results of this programme are discussed and the reductions in PM emissions from LD and HD diesel engines obtained by emulsions are compared to the effect on other regulated pollutants, PAHs and VOC.

Two different versions of diesel/water emulsions have been tested at the JRC:

- An emulsion for heavy duty applications currently marketed in several European countries and containing about 12% of water.
- Emulsions specially formulated for light duty applications containing about 6% of water. These emulsions are not currently marketed and the tests carried out by the JRC had the

objective of assessing the effect on emissions in view of their possible future introduction in the market.

The experimental programme consisted in emission tests carried out on three different light duty diesel vehicles (two passenger cars and one van) and on one heavy duty engine according to the current legislative procedures.

Concerning the HD engine, the tests have been carried out using an emulsion that can be normally found on the Italian market. The emissions of the engines measured using the emulsions were then compared to those measured feeding the engine with the standard diesel fuel that had been previously used to prepare the emulsion.

In the case of LD vehicles, four different fuels have been tested: two commercial diesel fuels and two diesel/water emulsions. The two standard diesel fuels, used as base fuels, differed for density, distillation curve, aromatic content and other properties; such fuels were also used to produce the two test emulsions.

The results of the emission tests carried out with the two diesel fuels and with the two emulsions were finally compared.

The main findings can be summarized as follows:

Heavy Duty Engine

- Over the European Stationary Cycle (ESC), the effect of the emulsion tested on CO and HC emissions was very different. While CO emissions decreased significantly (-32%), a slight increase of HC levels was noticed (+15%).
- NOx emissions were marginally reduced (-6%).
- The emulsion showed the largest effect on particulates: in terms of total mass, particulate emissions were reduced by -59%.
- Regarding the Polyaromatic Hydrocarbons (PAH) content, it was observed a minor reduction (-15%) of PM-associated benzo(a)pyrene toxicity equivalents (TEQ)

Light Duty Engine

- In all the test vehicles, the diesel/water emulsions led to a significant increase of CO (from a minimum of +9% to a maximum of +45%) and HC emissions (from +18% up to +49%). Despite the increase of CO and HC emissions the vehicles still met the related emission standards.
- NOx emissions showed a downward trend when the vehicles were fed with the emulsions: in any case the effects resulted to be quite small (NOx emissions are usually not very sensitive to fuel quality).
- As far as particulate emissions are concerned, with the emulsions a large decrease of the emission levels was noticed both over the urban part of the cycle and over the extra-urban part. In terms of total mass the reduction of emissions ranged from a minimum of -31% to a maximum of -45% over the whole NEDC cycle.

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- Concerning the unregulated emissions the use of non-commercial W/D emulsions containing 6% In LD diesel vehicles not only increased emissions of hydrocarbons but also the potential toxicity of the exhaust in terms of TEQ (+25%)
 - The effects of the emulsions on the emissions resulted to be influenced by the quality of the base diesel fuel to a very small extent. In fact, despite the extreme differences in the properties, the emulsions prepared with the two diesel fuels selected showed a very similar behaviour in terms of effects on emissions.

Conclusions

Based on the results of this study, and subject to all the limitations of the project plan and scope, the following can be concluded:

- the emulsion for heavy duty applications tested at the JRC is able to largely reduce particulate emissions over the ESC cycle (-59% in terms of total mass). The only drawback is a limited increase of HC emissions that may also correspond to an increase of the ozone formation potential. Nevertheless, taking into account the large effect on the particulate emissions and the reduction of the potential toxicity associated with the PAHs adsorbed on the particles, it can be concluded that the benefits seems to be higher than the potential negative effects.

This conclusion is in line with other studies as the very comprehensive one recently published by the California Environmental Protection Agency (CEPA); in this study emissions data were obtained from a wide range of conditions including engine type and model year, on and off road applications, and with and without after treatment emission controls. Although some pollutants of concern increased, the magnitude of their mass emissions resulted to be small compared to the decrease in mass emissions of PM. Thus, the authors of the assessment have evaluated the effect of these toxic emission increases and concluded that the absolute amount of these toxics in diesel exhaust is small and does not appear to be a significant cancer risk compared to diesel PM emissions. Hence, it seems safe to draw the same positive conclusions for the use of emulsion in the EURO 3 engine tested in the present study as in the risk assessment of the above mentioned Californian EPA study.

- Concerning the emulsions for light duty applications taken into consideration in this study, the results obtained have shown that besides the reduction of particulate emissions the emulsions lead to a significant increase of other regulated and unregulated pollutants. In other words, it seems that the use of emulsions in light duty engines worsen their global environmental performance; probably, due to the more sophisticated emission control technologies used on light duty vehicles compared to the heavy duty ones, the emulsions stop the engine from working in optimum conditions as the settings of the Engine Management Systems (EMS) are defined on the basis of tests performed with standard diesel fuels.

The large increase of VOC emissions with ozone formation potential and the higher potential toxicity of the particulate bound PAHs are negative effects that could impair the benefits associated with particulate emission reduction.

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

Il particolato e' fra i principali inquinanti che rendono a volte irrespirabile l'aria delle nostre città. Vari studi hanno oramai dimostrato gli effetti negativi del particolato e soprattutto della frazione con diametro inferiore ai 10 micron (PM10), sulla salute umana. A tale proposito, il costante aumento del numero di veicoli circolanti (più 49 per cento dal 1990 al 2003) e il crescente successo fra gli automobilisti dei veicoli diesel, notoriamente con emissioni di particolato più elevate rispetto ai veicoli a benzina, hanno certamente contribuito a limitare gli effetti benefici derivanti dalla disponibilità di veicoli sempre meno inquinanti grazie ai limiti di emissione via via più severi introdotti con le norme Euro 1, 2, 3 e 4 (entrate in vigore dal 1° gennaio 2005).

Alla luce di tali considerazioni una ulteriore riduzione delle emissioni dei veicoli è pertanto una misura certamente auspicabile. La Commissione Europea si sta già muovendo in questa direzione e a breve verranno proposti nuovi limiti ancor più stringenti: attualmente sono infatti in fase di discussione le norme Euro 5 per le autovetture ed Euro 6 per i veicoli pesanti. Per rispettare i nuovi limiti di emissione, le autovetture diesel dovranno quasi sicuramente essere equipaggiate con filtri per il particolato la cui efficienza di abbattimento va ben oltre il 90 per cento; per i veicoli pesanti la soluzione che verrà adottata sarà probabilmente diversa ma i filtri costituiranno comunque una importante opzione anche per essi, in particolare per i veicoli destinati all'utilizzo in aree urbane.

Tuttavia, prima che l'introduzione del filtro per il particolato dia gli effetti sperati in termini di miglioramento della qualità dell'aria, sarà necessario attendere che i veicoli dotati di tale sistema raggiungano una penetrazione nel mercato significativa: i benefici legati ad una qualunque nuova tecnologia motoristica o di post-trattamento dei gas esausti, anche se capace di abbattere in modo drastico le emissioni inquinanti, si concretizzeranno infatti pienamente solo dopo il completo rinnovo del parco veicolare circolante.

Assai diverso è il caso in cui si intervenga sulla qualità dei combustibili introducendone di riformulati o di alternativi: i benefici che ne possono derivare, seppure in genere molto più limitati, si concretizzano in tempi molto più brevi; sarà necessario attendere solamente che il nuovo combustibile sia disponibile su tutto il territorio e che venga utilizzato correntemente dai veicoli circolanti.

A tal proposito, fra le varie soluzioni proposte, le emulsioni gasolio/acqua hanno conosciuto negli ultimi anni una certa popolarità e hanno raggiunto una significativa diffusione quale combustibile per veicoli pesanti.

Tuttavia la diffusione delle emulsioni è stata accompagnata da non poche polemiche: a più riprese sono stati infatti avanzati dubbi sulla reale efficacia di questi prodotti nell'abbattere le emissioni inquinanti.

Per questo motivo si è sentita la necessità di un ulteriore studio sperimentale che, pur non pretendendo di essere esaustivo, cercasse di rispondere, per quanto possibile, alla domanda se le emulsioni gasolio-acqua rappresentano davvero un beneficio per la salute umana riducendo i rischi legati all'inquinamento dell'aria.

Tale studio è stato svolto in collaborazione dal Centro Comune di Ricerca della Commissione Europea di Ispra (VA) e dalla Regione Lombardia nell'ambito del Memorandum of Understanding siglato dai questi due enti.

Nel dettaglio, il ruolo del CCR è consistito nella definizione del programma sperimentale, nella esecuzione materiale delle prove e nella valutazione dei risultati. Per questo compito, fondamentali sono risultate essere le competenze e l'esperienza presenti all'interno della Unità Emissioni e Salute, la cui missione principale è quella di fornire supporto tecnico-scientifico alla Commissione Europea proprio sui temi inerenti le emissioni inquinanti da autoveicoli.

E' oramai assodato che per una valutazione piu' completa delle conseguenze sull'ambiente e sulla salute di una certa tecnologia è necessario andare oltre quanto prescrive la normativa vigente, la quale pone dei limiti di emissione solo in termini di massa totale per gli idrocarburi incombusti (HC), il monossido di carbonio (CO), gli ossidi di azoto (NOx) ed il particolato (PM). Infatti, la legislazione sulle emissioni inquinanti è stata sviluppata anche e soprattutto per rispondere ad una esigenza pratica quale l'omologazione dei veicoli. Lo studio del CCR è stato quindi progettato e condotto per poter investigare l'effetto delle emulsioni anche sui cosiddetti inquinanti non regolamentati, quelli che per il momento non sono soggetti ad alcuna norma; inoltre non ci si è limitati alla semplice misura della massa totale ma si è anche preso in considerazione l'aspetto qualitativo delle emissioni determinando, ad esempio, la quantità di idrocarburi poliaromatici (IPA o PAH) adsorbiti sul particolato. o sopra.

La sperimentazione svolta al CCR ha preso in considerazione sia emulsioni attualmente sul mercato e destinate ai veicoli pesanti, sia formulazioni sperimentali di emulsioni appositamente progettate per autovetture, comunque al momento non commerciabili per legge. Questi due tipi di emulsioni differivano fra loro per il contenuto d'acqua: 12% circa in quelle per veicoli pesanti e la metà in quelle destinate ai veicoli leggeri. A tal proposito, fondamentale è stata la collaborazione di una primaria azienda italiana che produce e commercializza emulsioni e che ha messo a disposizione la propria tecnologia ed i propri impianti per la preparazione dei combustibili di prova; le caratteristiche e le formulazioni di questi ultimi, scelte con l'obiettivo di garantire un risultato quanto più possibile valido da un punto di vista scientifico, sono state dapprima concordate fra questa azienda ed il CCR e quindi, una volta preparati, ricontrollate attraverso analisi eseguite da un terzo laboratorio indipendente. .

La sperimentazione è consistita in una serie di test di emissione condotti su autovetture e su un motore heavy duty rappresentativi delle tecnologie motoristiche attualmente più diffuse.

I risultati ottenuti hanno innanzitutto evidenziato un comportamento molto diverso fra le emulsioni sperimentali per autovetture e quelle per motori pesanti che, oltre a dipendere dalla diversa formulazione delle emulsioni, probabilmente riflette anche le diversità nella tecnologia motoristica fra motori Light Duty e motori Heavy Duty. I principali risultati possono essere così riassunti:

Heavy Duty Engine

L'effetto quantitativamente più importante legato all'impiego delle emulsioni ha riguardato le emissioni di particolato con una riduzione della massa totale del -59%. Ciò è stato accompagnato anche da una significativa riduzione delle emissioni di CO (-32%) e da una diminuzione tendenziale delle emissioni di NOx (-6%).

Di contro si è osservato un limitato aumento delle emissioni di idrocarburi incombusti (+15%) che però, partendo già da livelli molto bassi, si sono comunque mantenute ampiamente al di sotto dei limiti.

Passando agli inquinanti non regolamentati, le analisi chimiche svolte sul particolato hanno evidenziato una diminuzione dell'indice di tossicità equivalente degli IPA adsorbiti sulle particelle.

Per quanto riguarda la potenza erogata invece, le prove condotte su motore hanno permesso di evidenziare che a parità di posizione dell'acceleratore, con l'emulsione vi è una perdita di

potenza pari all'incirca al contenuto di acqua. Nei veicoli pesanti vi è dunque una riduzione della potenza massima erogabile dal motore che è circa del 10-12%; quanto sopra significa altresì che se su strada si vuol mantenere la stessa velocità, si deve iniettare nel cilindro all'incirca la stessa quantità di gasolio. In altre parole, a parità di velocità, si avrà un consumo di emulsione superiore di circa il 10-12% rispetto al gasolio tal quale.

Light Duty Vehicles

I risultati relativi alle emulsioni sperimentali per autovetture hanno invece mostrato degli effetti molto più contrastati: a fronte di una importante riduzione delle emissioni di particolato (da un minimo del -31% ad un massimo del -45%) si sono osservati aumenti non trascurabili delle emissioni di CO (da +9 a +45%) ed HC (da +18% a +49%).

Per ciò che riguarda gli NOx non si sono invece osservate variazioni di rilievo.

La qualità del gasolio di base è risultata abbastanza ininfluyente sul comportamento delle emulsioni, almeno per quel che riguarda le emissioni regolamentate. Prendendo in considerazione inquinanti non regolamentati come i poliaromatici adsorbiti sul particolato, si nota invece una netta differenza fra i due gasoli che si riflette poi anche sul comportamento delle emulsioni.

Inoltre, per quanto riguarda gli IPA veicolati dalle particelle, con le emulsioni si è notata una variazione del profilo di emissione degli stessi, con un arricchimento in quelli potenzialmente più tossici: questo si è tradotto in un aumento non trascurabile del TEQ. In altre parole, le particelle emesse, pur in numero inferiore, sono risultate potenzialmente più tossiche in termini assoluti.

Per quanto riguarda altri aspetti quali il numero e la distribuzione granulometrica delle particelle, le misure eseguite hanno mostrato che l'abbattimento della massa totale si traduce in una riduzione del numero delle particelle e soprattutto di quelle aventi diametro maggiore. Infine, le analisi condotte sugli idrocarburi incombusti per identificarne i singoli componenti hanno permesso di stabilire che l'emulsione non ne modifica in maniera sostanziale il profilo: alle più elevate emissioni di HC, corrisponde quindi un aumento percentualmente equivalente della formazione potenziale di ozono.

Conclusioni

Una prima conclusione è che certamente le emulsioni per autovetture nella formulazione sperimentale provata necessitano, quanto meno, di ulteriore sviluppo prima di poter rappresentare una valida opzione per l'abbattimento delle emissioni inquinanti. Ciò del resto è stato correttamente riconosciuto anche dalla azienda che le ha proposte. Nei motori delle autovetture, forse perché più sofisticati e più vicini ai limiti tecnologici per quanto riguarda il controllo delle emissioni, le emulsioni sembrano determinare un allontanamento dalle condizioni di funzionamento ottimali con gli effetti negativi che forse potrebbero controbilanciare o addirittura sovrastare quelli positivi. Non va però nascosta la difficoltà di fare un bilancio di questi effetti avendo come riferimento il rischio per la salute umana; e' pertanto davvero arduo concludere se, alla fine, vi è un peggioramento o un beneficio netto anche perché tutto ciò dipende sicuramente dalle condizioni ambientali in cui vengono ad essere

utilizzati questi prodotti. Ad esempio, in un'area in cui il problema principale è l'ozono le emulsioni per autovetture, almeno nella formulazione valutata, probabilmente provocherebbero più problemi di quanti ne risolvono.

Diverso invece è il discorso per le emulsioni destinate ai veicoli pesanti; in questo caso, molto probabilmente per le caratteristiche proprie dei motori Heavy duty, sembrano venire meno la maggior parte delle criticità osservate nei motori più leggeri e dal punto di vista dell'impatto sull'ambiente l'immagine che emerge dalla sperimentazione condotta è sostanzialmente positiva. Infatti l'abbattimento notevole delle emissioni di particolato riscontrato non è accompagnato dagli importanti effetti negativi "collaterali" osservati sulle autovetture. .

Questo giudizio è tra l'altro in linea con le conclusioni che l'Agenzia per la Protezione dell'Ambiente californiana (CEPA) ha tratto da uno studio su prodotti analoghi, esprimendo un parere positivo; in particolare la CEPA ha concluso che la riduzione del rischio per la salute umana legato alle minori emissioni di particolato controbilancia ampiamente i potenziali rischi associati all'incremento degli idrocarburi incombusti e della più alta formazione di ozono che ne può conseguire.

Va infine ricordato che la sperimentazione condotta dal CCR ha principalmente riguardato l'effetto delle emulsioni sulle emissioni inquinanti e ha volutamente tralasciato di considerare altri aspetti, seppure di importanza non secondaria, quali gli effetti sulle prestazioni e sul buon funzionamento (affidabilità) del motore e sulla guidabilità del mezzo. Nulla quindi si può dire a tale proposito oltre quanto riportato dalle aziende che producono le emulsioni.

2 Diesel fuel/water emulsions: introduction

The positive effect on pollutant emissions of water injected in the combustion chamber of internal combustion engines has been known since many decades. However, only recently the technological development has made possible to exploit that. In fact, as well known, water and diesel fuel are miscible to a very limited extent (only up to a few hundreds ppm). Therefore, any mixture of diesel and water will evolve toward a separation of the two phases. Other approaches, like producing the emulsion just before the injection, require heavy modifications to the engine and an additional tank for the water; that represent a technical barrier for such options.

However, using special additives (emulsifying agents) it is possible to create a diesel/water emulsion stable for an adequate period of time. Such emulsions have been proposed some years ago as fuels capable of reducing particulate emissions from diesel vehicles and since then they have gained some popularity.

According to the most shared theories, the emulsions influence emissions via several mechanisms. One of the most important mechanisms is believed to be the micro-explosion of the water droplets; the droplets, injected in the combustion chamber together with the diesel fuel, are in unstable conditions because of the high temperature and pressure levels. As a consequence, the droplets undergo a very fast boiling process that can be assimilated to a micro-explosion. This phenomena improves the nebulization of the diesel fuel and the mixing of it with air. The result of that is the reduction of the rich areas where, due to a low air/fuel ratio, the diesel fuel cannot easily burn and the soot is formed (see fig. 1).

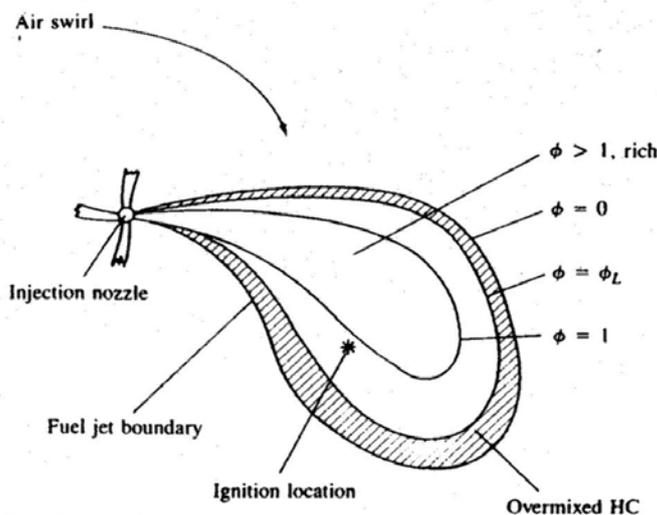


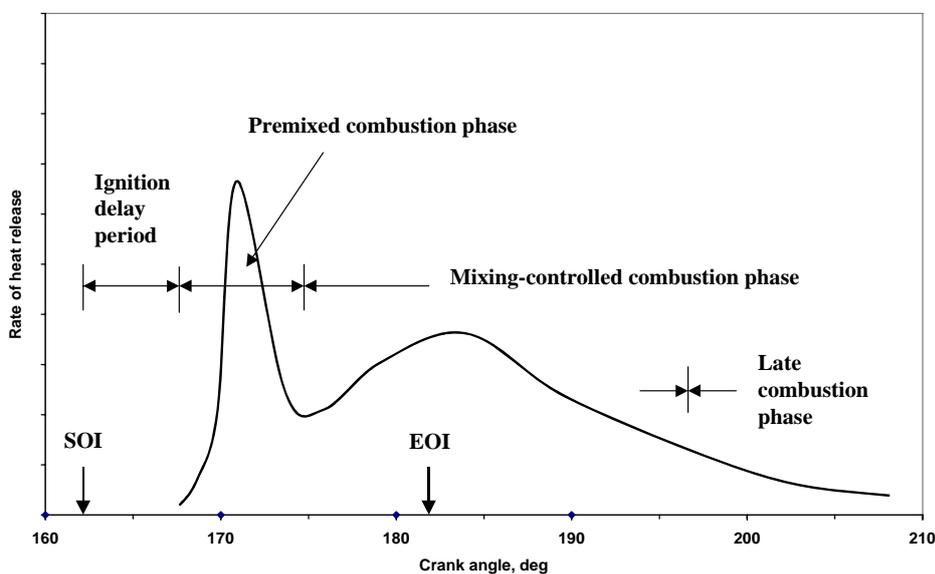
Fig. 1 – Air/fuel ratio distribution after diesel injection in the combustion chamber

Another consequence of the use of the emulsions is an increased ignition delay. The ignition delay is the period of time between the start of the fuel injection and the start of the combustion (see fig. 2); the ignition quality of the fuel, in general measured by the cetane number, is one of the main parameter influencing the ignition delay. The emulsions usually lead to a significant increase of the ignition delay, partially because of their lower cetane number compared to the

standard diesel fuel. A longer ignition delay means a different profile of the combustion process, typically consisting of two phases in the diesel engine: the premixed combustion phase and the mixing-controlled combustion phase. The soot is mainly formed during the latter phase, when the combustion is controlled by the rate at which the mixture air/fuel becomes available for burning; in other words, during this phase the rate of burning is controlled by the fuel vapour/air mixing process.

Within certain limits, the longer the ignition delay, the larger the amount of fuel that burns during the premixed phase with almost zero soot formation. Therefore, also in this case the emulsions influence the combustion process in a way that leads to a reduced formation of particulates. However, the longer ignition delay means also a larger amount of fuel that over-mixes with air beyond the lean combustion limit that is one of the major sources of unburned hydrocarbons.

Fig. 2 – Typical evolution of combustion in a diesel engine.



Other effects of the emulsions on the combustion process that affect in different ways the emissions are the following:

- Increased duration of the injection. In comparison to a standard diesel fuel, the amount of emulsion that has to be injected to obtain the same power output from the engine is much larger. In particular, the amount diesel fuel contained in the emulsion injected in the combustion chamber has to be about the same as in the case of the use of the standard diesel fuel. As a consequence, in the same operating conditions, the duration of the injection is longer and that means that a larger amount of fuel is injected during the late phase of the combustion contributing to the increase of HC emissions.
- Due to the higher thermal capacity of the water, the temperature in the combustion phase should be a bit lower than with the standard diesel fuel. That has a positive effect on the NO_x emissions.
- The injection of water in the combustion chamber seems to increase the concentration of the OH radicals; that increases the rate of soot oxidation and contributes to the reduction of particulate emissions.

The mechanisms above described explain quite satisfactorily why the emulsions in general are effective in reducing particulate emissions; however, it appears quite clearly that one drawback of the use of the emulsions is an increase of unburned hydrocarbon emissions.

Emulsions for heavy duty applications

3 Experimental work

The experimental work consisted in emission tests carried out on a heavy duty engine installed on an engine test bench. The tests were carried out according to the current European legislation; the emissions measured with a standard diesel fuel were compared to those obtained with the water/diesel emulsion prepared using the same standard diesel fuel.

3.1.1 Test Engine

The heavy duty engine used for the experimental programme is representative of the typical engines used in Europe to power heavy duty vehicles like buses and trucks. Furthermore the model is a quite widespread one and many heavy duty vehicles on the road are equipped with such engine type.

The main features of the test engine are listed in the following table:

Tab. 1

	HD ENGINE
Emission level	EURO 3
Displacement (cm ³)	10308
Max. Power (kW @ rpm)	316 @ 2100
Inertia Class (kg)	-
Cylinder	6
Aspiration	Turbocharged
Combustion Type	DI
Injection System	PDU
EGR	No
Oxidation Catalyst	No
Year	2003

The engine was certified to meet Euro 3 emission limits; that was confirmed by the tests carried out using the standard ESC cycle and the base fuel (see table 2), despite the fact the fuel was a commercial one and not a certified reference fuel as required by the certification procedure.

Tab 2- Engine emissions vs Euro 3 limits.

ESC cycle	HC (g/kWh)	CO (g/kWh)	NO _x (g/kWh)	PM (g/kWh)
Euro 3 limits	0.66	2.1	5.0	0.1
Engine emissions	0.11	0.75	4.16	0.073

3.1.2 Test fuels

The two test fuels were a diesel/water emulsion for heavy duty application available on the market in Italy and a standard diesel fuel; the latter was the same used to produce the emulsion. Both the fuels were supplied by an Italian company producing and marketing emulsions.

The test fuels were analysed by a third laboratory and the main properties of them are reported here below (table 3) :

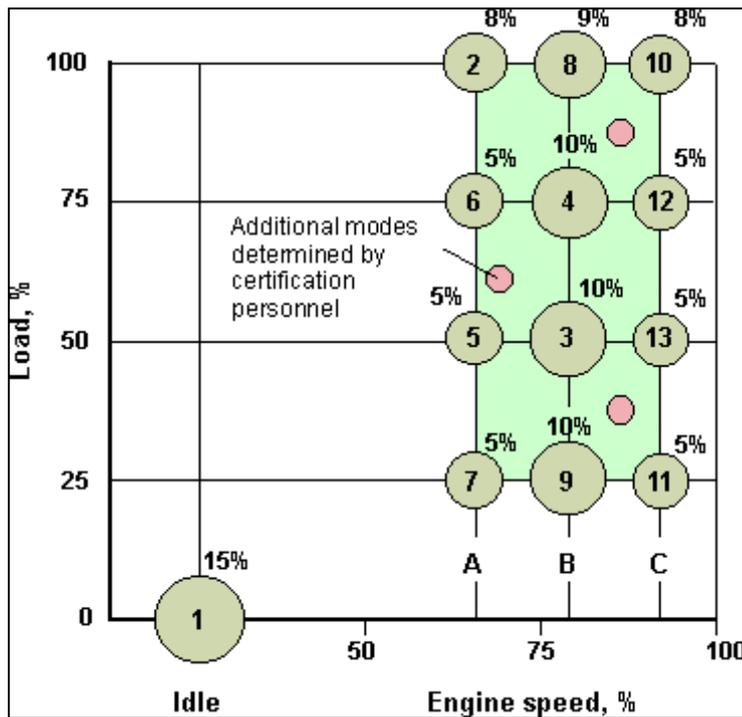
Tab. 3

	Unit	Standard Diesel Fuel	HD Emulsion
Density @ 15 C	kg/l	0.826	0.848
Sulphur Content	mg/kg	<10	-
CFPP	° C	- 3	- 7
Cetane Number		56.2	53.5
Distillation			
10 % vol	° C	242	n.d.
50 % vol	° C	281	n.d.
90 % vol	° C	348	n.d.
95 % vol	° C	367	n.d.
Cetane improver, ENN		0	1986
Water	% v/v	0	12.0
Total Aromatics	% v/v	19.5	17.2
Polyaromatics	% v/v	2.7	2.4

3.1.3 Emission tests

The emission tests were carried out on a dynamic engine test bench according to the European Stationary Cycle (ESC) described in the figure 3. Regulated emissions (HC, CO, NOx and Particulates) were measured following the legislative measuring procedures.

Fig. 3



1. The high speed n_{hi} is determined by calculating 70% of the declared maximum net power. The highest engine speed where this power value occurs (i.e. above the rated speed) on the power curve is defined as n_{hi} .
2. The low speed n_{lo} is determined by calculating 50% of the declared maximum net power. The lowest engine speed where this power value occurs (i.e. below the rated speed) on the power curve is defined as n_{lo} .
3. The engine speeds A, B, and C to be used during the test are then calculated from the following formulas:

$$A = n_{lo} + 0.25 (n_{hi} - n_{lo})$$

$$B = n_{lo} + 0.50 (n_{hi} - n_{lo})$$

$$C = n_{lo} + 0.75 (n_{hi} - n_{lo})$$

A first block of tests was carried out with the standard diesel fuel to check the emission performance of the engine that met Euro 3 standards which it had been certified for.

Then, a second block of tests was carried out with the diesel/water emulsion; in this case it was necessary to modify the test cycle since the maximum power of the engine was significantly lower with the emulsion than with standard fuel.

As shown in the figure 4, the ESC cycle for the emulsion, derived following the legislative procedure, is quite different compared to the one used with the standard diesel fuel. In particular, both the rpm and the torque values are different and the latter are significantly lower.

For this reason, to allow a more direct comparison of the emission performance of the two test fuels, a third block of tests was carried out with the standard diesel fuel but using the ESC cycle operating conditions defined for the emulsions.

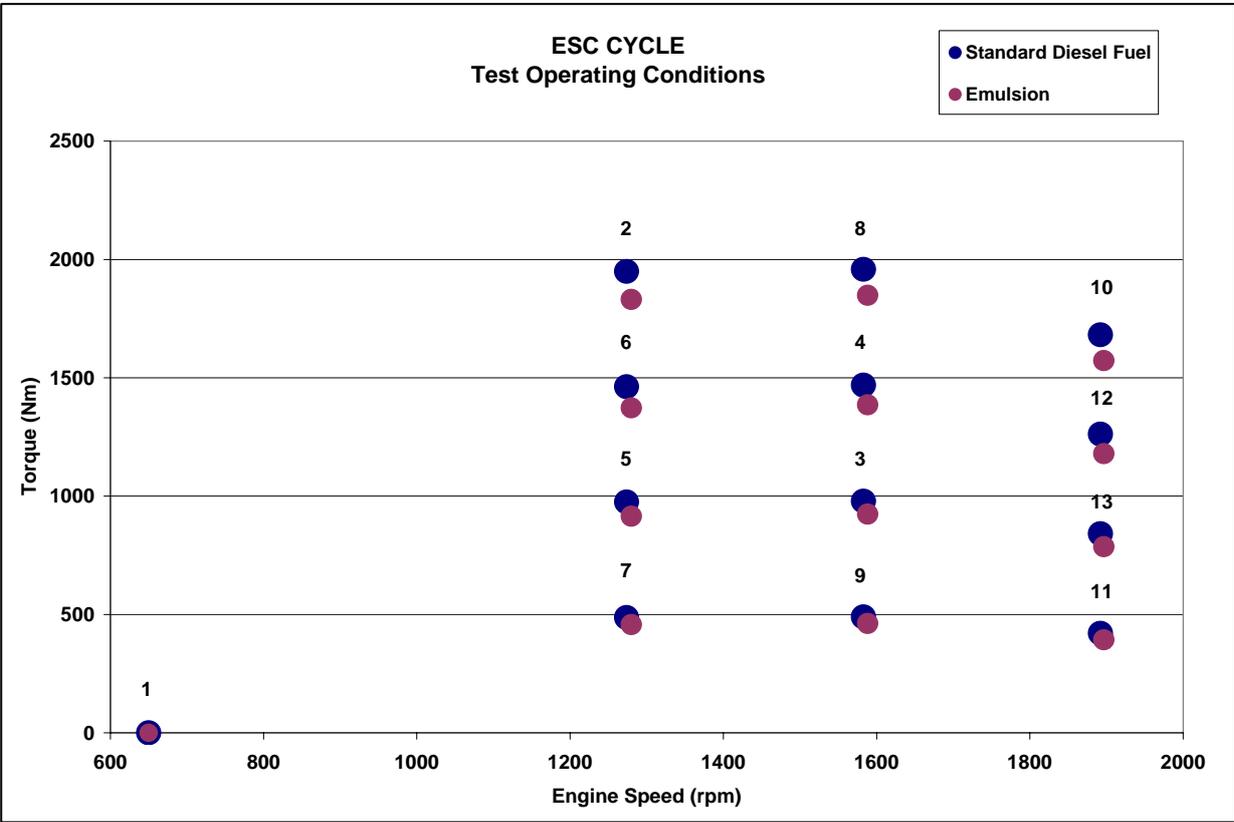
The detailed test sequence is described in table 4.

Tab. 4

Test n.	1-2-3-4-5-6-7	8-9-10-11	12-13-14
Fuel	Base Fuel	Emulsion	Base Fuel*

*Same operating conditions as emulsion

Fig. 4



3.1.4 Instrumentation details

Regulated pollutant emissions were measured using an engine test bench equipped with a suitable brake and a conventional full flow dilution system based on the CVS concept and equipped with a secondary dilution tunnel.

The main features of the brake, of the dilution tunnel and of the analysers are listed here below:

Dilution tunnel:

- Full flow dilution tunnel
- Secondary dilution tunnel for particulate mass measurement
- Four critical orifices that allow to select the most appropriate flow rate from a minimum of 40 m³/min to a maximum of 140 m³/min.

Brake:

- Dynamic type, manufactured by AVL AFA
- Power: 80-500 kW
- Maximum speed: 3500 rpm
- Maximum torque: 2375 Nm

The brake and the engine are operated by means of a AVL PUMA OPEN System.

Analysers for gaseous emission measurement:

- CO: ABB NDIR analyser.
- NOx: Ecophysys chemiluminescence analyser.
- HC: ABB FID analyser.

Particulate mass:

- particulate samples were collected according to the legislative procedure for diesel engines. The sampling point is located on the secondary dilution tunnel. The particulate total mass was determined by weighing using Pallflex 70 mm T60A20 filters.

4 Results

4.1 Regulated Emissions

The tests, performed according to the current legislation and over the European Stationary Cycle (ESC), exhibited a very good repeatability as shown in the figures 5-8. The first block of bars (blue colour) shows the results of the tests carried out with the standard diesel fuel (base fuel) and the standard ESC cycle. In order to check the stability of the engine and the repeatability of the measurements seven tests were performed.

The second block of bars (magenta colour) is referred to the tests in which the engine was fuelled with the emulsion and performed using the modified ESC test cycle as described in the chapter 3.1.3. Finally, the green bars represent the tests performed with the standard diesel fuel but using the same ESC cycle as used for the emulsion. Therefore, the results obtained with the emulsion have to be compared to the third set of bars.

To investigate the effect of the emulsion on the emissions, the mean values of the levels measured with the standard diesel fuel and with the emulsion have been calculated and compared. The mean values are reported in the figures 9-10.

Fig. 5

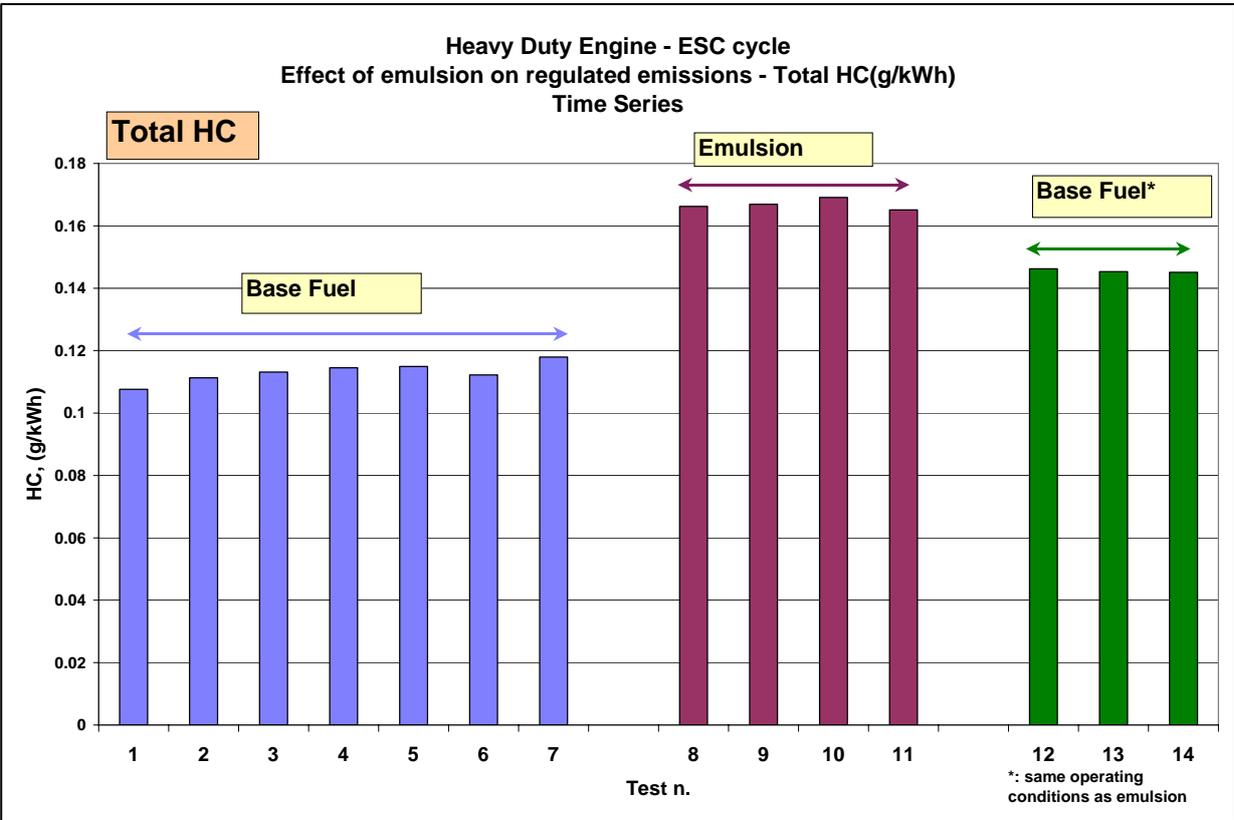


Fig. 6

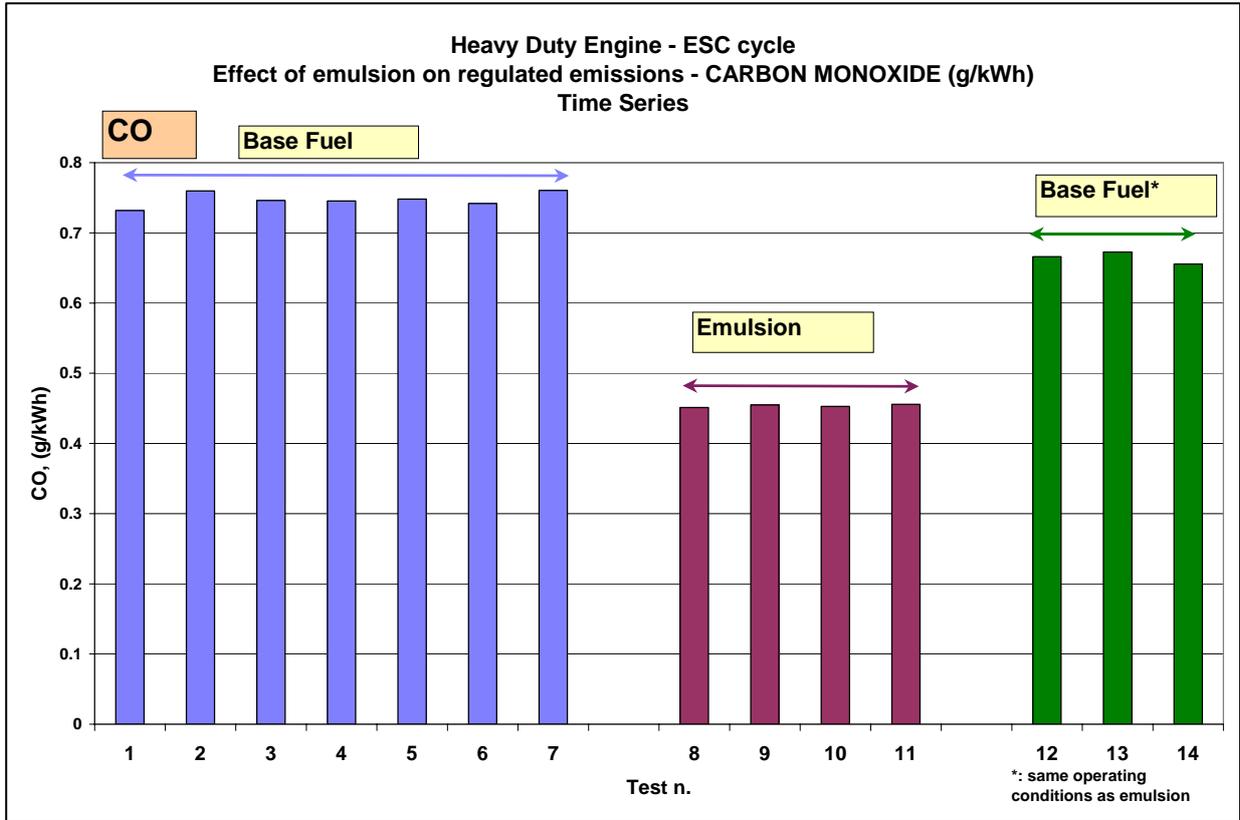


Fig. 7

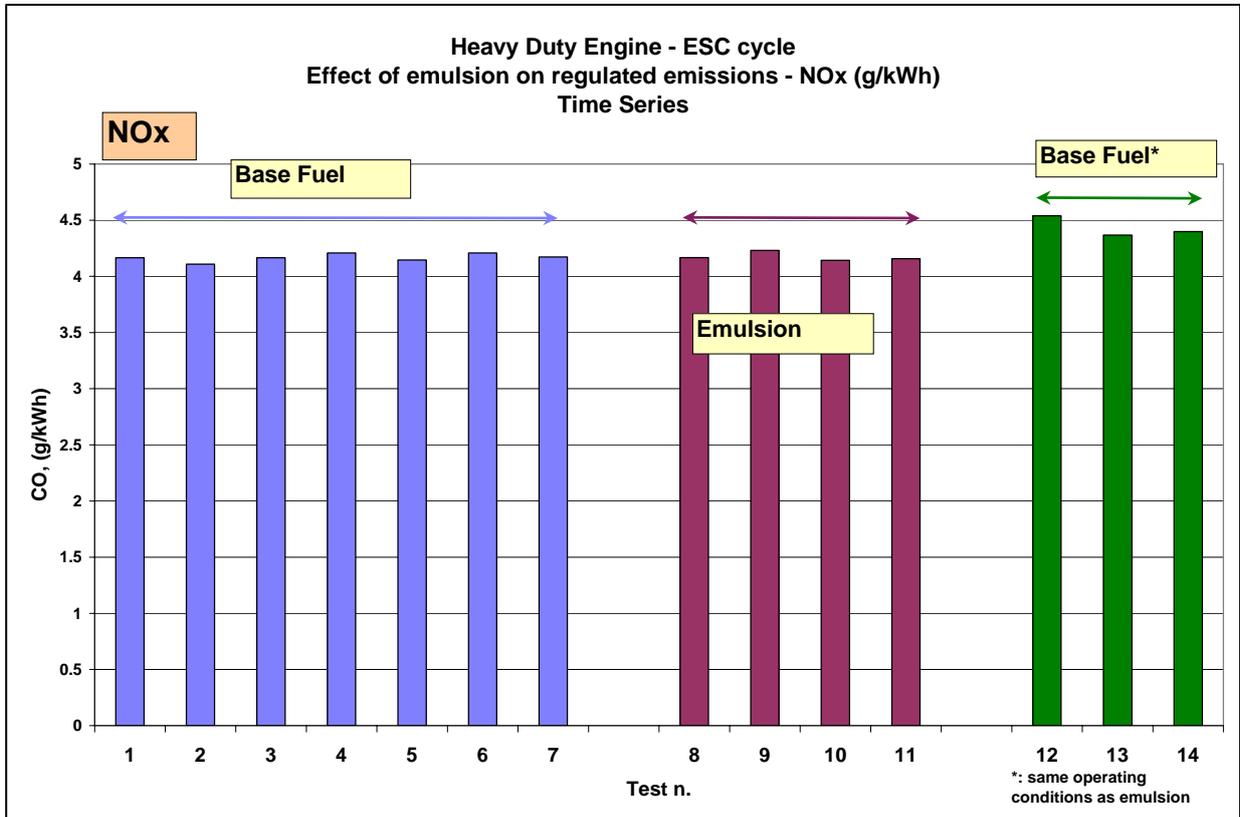


Fig. 8

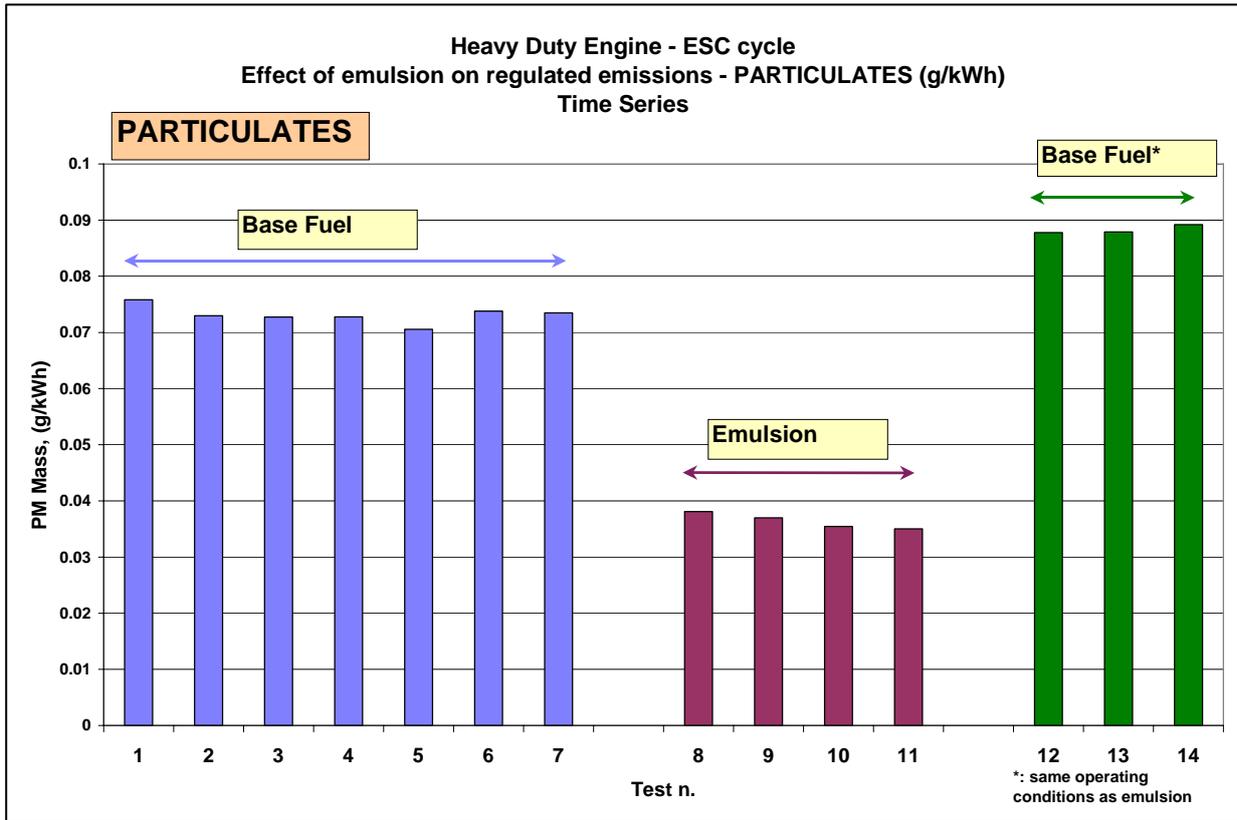


Fig. 9

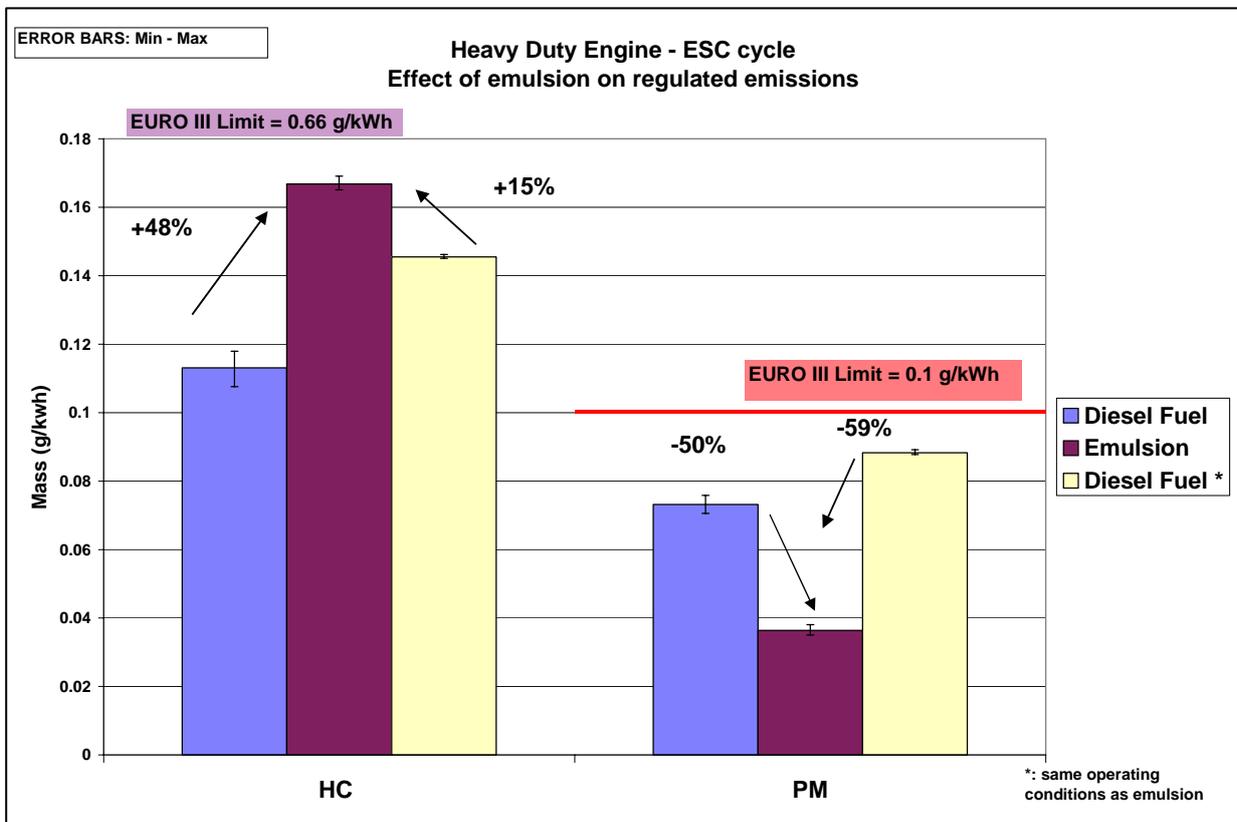
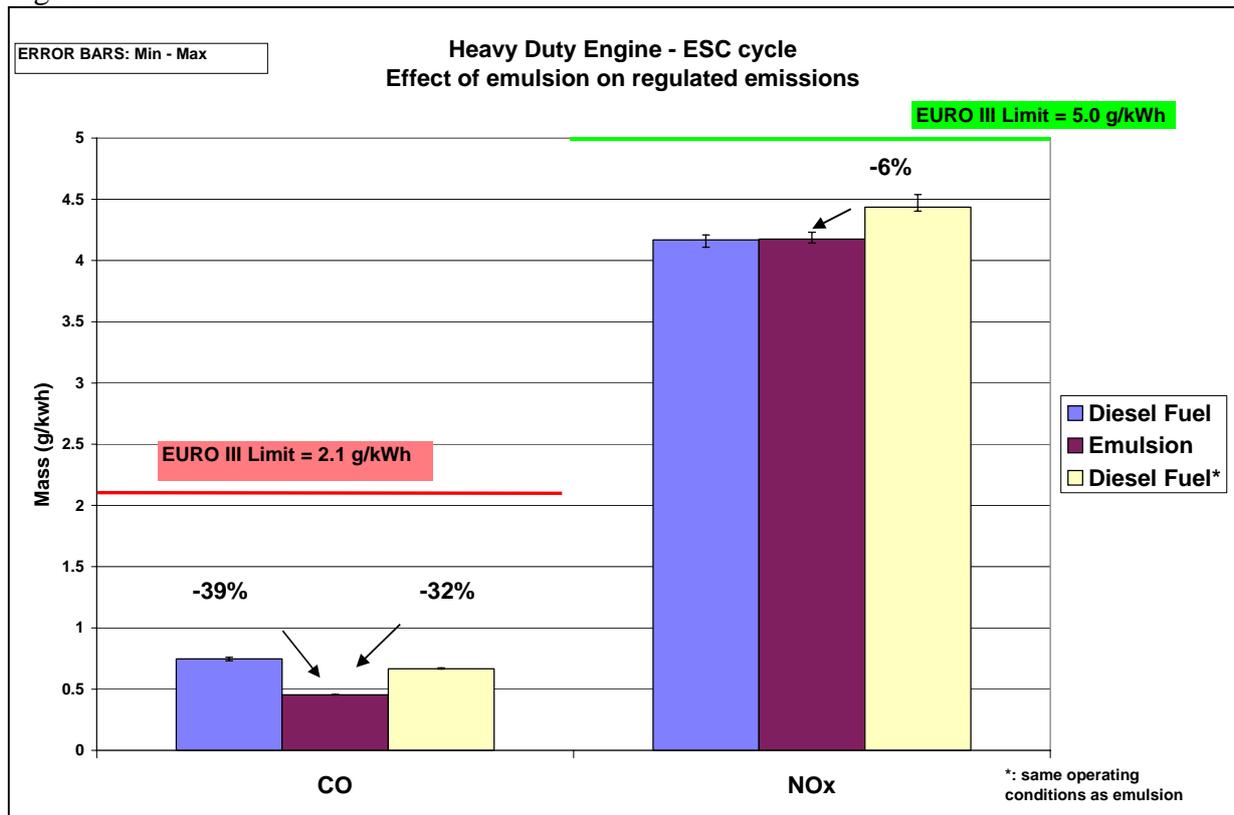


Fig. 10



Gaseous Emissions

Compared to the standard diesel fuel, the use of the emulsion led to a significant decrease of CO emissions over the ESC cycle while HC emissions increased. The comparison between the mean values (same operating conditions) shows an increase of 15% for HC emissions (fig. 9) and a decrease of -32% for CO (fig. 10)

In any case, the engine exhibited CO and HC emission much lower than the limits for which it had been certified. For example, the mean value of the HC emissions over the standard ESC cycle was 0.11 g/kWh versus a limit of 0.66 g/kWh.

Therefore, despite the emulsion increased by 48% the HC emissions compared to the standard ESC cycle (base fuel), the emission level remains well below the limit (0.17 g/kWh versus 0.66 g/kWh).

NOx emissions (Fig. 10) showed a downward trend with the emulsion but the percentage variation was quite small (-6%).

Particulates

The emulsion had the largest effect on particulate emissions: comparing the values measured with the emulsion and the standard diesel fuel in the same operating conditions, particulate

emissions were reduced by -59% in terms of total mass (fig. 10). Compared to the particulate emission measured over the standard ESC cycle the emissions were anyway reduced by 50%.

These data clearly suggest that the emulsion is very effective in reducing particulate mass, while the impact on the other regulated pollutants is much more limited.

4.2 Unregulated emissions: chemical composition of particulates

A quick overview to the previous pages reveals that water /diesel emulsions containing 12% water can reduce PM (-59%), CO (-32%) and, also marginally, NO_x emissions in a EURO-3 HD engine. Only a slight increase on hydrocarbons emissions (+15%) has been found. Our next argument will be to find out if this W/D emulsion may also have a positive effect on the chemical composition of the particle matter emitted by a HD engine.

Total particulate mass was measured using Pallflex 70 mm T60A20 filters which are weighed before and after the emission test. The particulate collected on these filters commonly consist of 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 is grabbing our attention is the amount of potentially harmful organic compounds adsorbed on the particles.

In this report, sixteen priority Polycyclic Aromatic Hydrocarbons (PAH) recommended by EPA because of their mutagenic and, in some cases, carcinogenic properties have been analyzed in particulate matter from vehicle/engine exhaust emissions. All these PAHs are toxicologically relevant organic compounds that are regularly absorbed onto the particles.

Polycyclic Aromatic Hydrocarbons (PAH) are ubiquitous environmental contaminants that are formed by the incomplete combustion of organic materials such as wood and fossil fuels and therefore also present in respirable particulate matter from ambient air and primary sources [1,2].

PAHs molecules are made up of three or more benzene rings, at least two of which are fused with two neighbouring rings sharing two adjacent carbon atoms. PAHs form a large heterogeneous group, but the most toxic compounds of this family known to date are PAHs molecules that have four to seven rings, which have also been included in this report.

There are currently no EU Directives or other guidance to member states which bear directly on either emissions or air quality objectives of PAHs but, European Commission has prepared a proposal for a Directive [COM (2003) 423 final; 2003/0164] that will cover the remaining pollutants listed in Annex I of Air quality directive 96/62/EC, including PAHs.

One of the first chemicals of this family which has been recognized as carcinogenic is the Benzo[a]pyrene (BaP) which has been considered in this proposal as a suitable marker due to its stability and relatively constant contribution to the carcinogenic activity of particle-bound PAHs.

4.3.1. Experimental details

The principal stages of PAHs determination are: Sampling, extraction, clean up and analysis. The method used in this work has been developed in our laboratories and based on the EPA method TO 13 and ISO/DIS 12844. Due to the lack of legislation of this kind of measurements in the emissions regulations, the complete methodology used for the analysis of PAHs in exhaust filters is based on analytical methods that are very well-known for the analysis of these compounds in in PM proposed by the Air Quality Legislation.

Sampling was performed in coincidence with the total particulate mass measurement according the legislative procedure (see regulated Particle mass); the same filter used to collect the sample and measure the particulate emissions in terms of total mass was the analyzed to characterize particulates from a chemical point of view.

Sample extraction and clean-up

Filters containing particulate from engine exhaust were extracted in an automatic Soxhlet extractor for 2 h with dichloromethane. The extracts were evaporated to nearly dryness with a “Turbo Vap” System. After reducing the volume, the extract was transferred in a SPE column for the clean-up procedure. The residue including the PAHs 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 hexane/dichloromethane (60:40) and successively with acetonitrile/TEM. Both second and third fraction were collected together. The eluate was evaporated almost to dryness and redissolved in Toluene and analyzed by GC-MS.

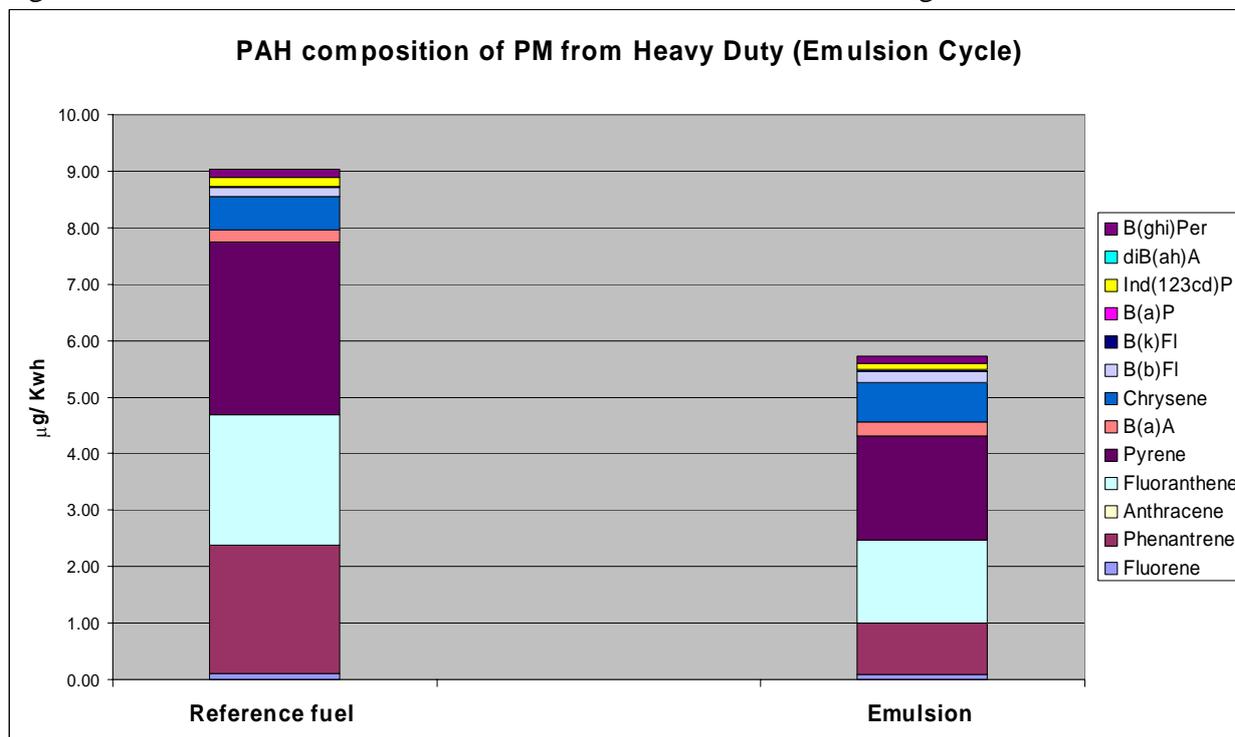
GC-MS analyses were performed with a 6890 HP Series Plus + GC system equipped with an auto-injector 7683 HP Series. The mass spectrometer was a 5973 HP Mass Selective Detector equipped with both Electron Impact and Chemical Ionisation sources. The column used was a HP-5MS fused silica capillary column,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

Separation conditions used: injection volume 2 μL in pulsed splitless mode; carrier gas helium at a constant flow rate of 1.0 mL/min; injector temperature 250 $^{\circ}\text{C}$. Run time for one analysis is 29.5 min. EI ionisation was employed at 70 eV. Pressure inside the source is $1.9 \cdot 10^{-5}$ Torr. MS source temperature was set to 230 $^{\circ}\text{C}$; MS quadrupole temperature: 150 $^{\circ}\text{C}$ and GC/MS interface temperature: 280 $^{\circ}\text{C}$.

By means of this experimental procedure, a significantly number of individual PAHs has been identified and they are found to be in the same range of concentration as those found by other authors [3,4]

In Figure 11 we can see the results for the tests with the two different fuels, the Reference fuel and the emulsion. The results shown the quantitation for thirteen PAHs of the 16 PAHs recommended by EPA that had been analysed. The most volatile of the 16 EPA priority PAHs were not quantified in PM in the present study since these compounds display a low recovery in our analytical procedure and are expected to partition mainly into the gas-phase of the exhaust.

Fig. 11 Effect of W/D emulsion on emissions from an EURO-3 HD engine



We have expressed these measurements in concentration for each PAH in: **ng PAH/kWh**. The mass of PAHs emitted per kWh can be calculated just by means of the same formula used to calculate the particulate total mass. In order to enable the relative toxicity of such a mixture of compounds to be expressed as a single number, the concept of **Toxicity Equivalence (TEQ)** has been applied.

4.3.2. Overall toxicity of the Mixture

Toxic Equivalency Factor (TEF) is a measure of relative toxicological potency of a chemical compared to a well characterized reference compound. TEFs can be used to sum the toxicological potency of a mixture of chemicals which are all members of the same chemical class, having common structural, toxicological and biochemical properties. The TEF approach has been extensively used for hazard assessment of different mixtures of for chlorinated dibenzodioxins and dibenzofurans and for polycyclic aromatic hydrocarbons. The concept of TEF (Toxicity Equivalence factor) has been proposed to facilitate both human and ecological risk assessment and associated to management decisions.

PAHs usually occur as a complex mixture of congeners and in this report, Toxicity Equivalence (TEQ) are based on the international toxic equivalents scheme. The toxicity of each congener is given a toxic equivalent factor (TEF) rating. The most toxic congener Benzo(a)pyrene is rated as 1. Other congeners are rated between 0 and 1, depending on their relative toxicity. [5,6]

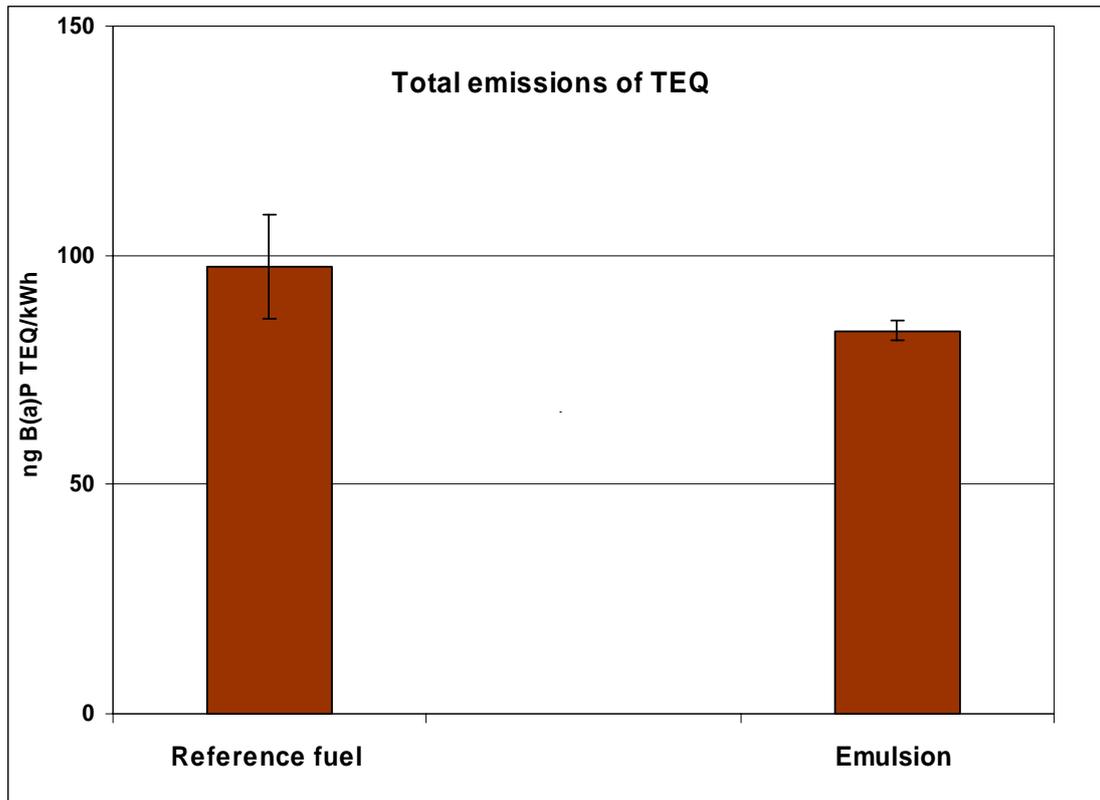
The potential toxicity of a sample is calculated in two steps. Firstly, the concentration of each congener in the sample is multiplied by its TEF. Next, the total toxicity is calculated by adding together the contributing toxicity of each congener. This standardizes the measurement so it can be used to compare results with other sites and international levels.

The overall toxicity or toxic Equivalents (TEQs) of a Mixture are defined by the concentration of individual compounds (Ci) in a mixture times their relative potencies or TEFs.

$$TEQ = \sum [C_i] \times TEF_i$$

By applying this concept and observing the results obtained during the test performed with the reference fuel and the one performed with the emulsion, we could detect that the trend is the same we found for the PAHs concentration. That means that the use of the 12% W/D emulsion in HD EURO 3 vehicles has a positive effect in the quality of the emissions in terms of toxicity since a clear improvement is observed during both cycles (Fig. 12, test average \pm 95% confidential interval).

Fig. 12



5 Conclusions

The emulsion for heavy duty applications tested at the JRC is able to largely reduce particulate emissions over the ESC cycle (-59% in terms of total mass). The only drawback is a limited increase of HC emissions that means also an increase of the ozone formation potential. Nevertheless, taking into account the large effect on the particulate emissions and the reduction of the potential toxicity associated with the PAHs adsorbed on the particles, it can be concluded that the benefits seems to be higher than the potential negative effects.

This conclusion is in line with other studies as the very comprehensive one recently published by the California Environmental Protection Agency (CEPA). In this study emissions data were obtained from a wide range of conditions including engine type and model year, on and off road applications, and with and without after treatment emission controls. With the investigated commercial W/D emulsion (20% water) emissions of PM and NO_x were reduced on average, by 58 percent and 14 percent, respectively and ozone precursor reactive organic gas (ROG) emissions were increased by 87 percent; In a multi-media assessment of these results it has been pointed out that the emissions of ROG by use of the W/D emulsion are about 29 percent of the NO_x emissions in diesel exhaust, which in other words means that for each ton ROG increased, NO_x will be reduced by 3.4 tons (CEPA). Thus, when evaluating the emission effects on an absolute basis, mass emission reductions for NO_x by use of emulsions was greater than mass emission increases of total HC. Increases in emissions of some toxic species such as formaldehyde, acetaldehyde, benzene, toluene, ethyl benzene, xylenes, 1,3-butadiene, and some PAHs by use of the 20% W/D emulsion were also mentioned (CEPA). Although the increase of these pollutants is of concern, the magnitude of their mass emissions is small compared to the decrease in mass emissions of PM. Thus, the authors of the assessment have evaluated the effect of these toxic emission increases and concluded that the absolute amount of these toxics in diesel exhaust is small and does not appear to be a significant cancer risk compared to diesel PM emissions (CEPA). Hence, not only for the for the point of view of PM and NO_x but also PAHs it seems safe to draw the same positive conclusions for the use of emulsion in the EURO 3 engine tested in the present study as in the risk assessment of the above mentioned Californian EPA study, which was based on a wide range of conditions including engine type and model year.

Emulsions for Light Duty application

6 Experimental work

6.1.1 Test fleet

The test fleet consisted of 3 diesel vehicles: 2 passenger cars and 1 van for passenger transportation. The vehicle differed for model, engine technology and odometer reading. The main data of the vehicles are listed here below (table 5):

Table 5

Vehicle Type	Passenger car		Van
	PC (A)	PC (F)	VAN (M)
Emission level	EURO 3	EURO 3	EURO 3
Category	M1	M1	N1, Class III
Displacement (cm ³)	1896	1910	2148
Max. Power (kW @ rpm)	77 @ 4000	85@4000	80
Inertia Class (kg)	1265	1265	1980
Cylinder	4	4	4
Max. Torque (Nm @ rpm)	250 @ 1800	255 @ 2000	
Aspiration	Turbocharger	Turbocharger	Turbocharger
Combustion Type	DI	DI	DI
Injection System	Unit Injector	Common Rail	Common Rail
EGR Y (yes) N (no)	Y	Y	Y
Oxidation Catalyst Y(yes) N(no)	Y	Y	Y
Year	2003	2003	2003
Odometer reading	46340	101295	63000

6.1.2 Test fuels

The test matrix comprised two commercial diesel fuels (Tab.6) and the two corresponding emulsions (Tab. 7). The two diesel fuels had very different properties: Fuel 1 had a density close to the upper limit of the legislative range (0.820-0.845) while Fuel 2 close to the lower limit. Both fuels had a low sulphur content but it was lower in the case of Fuel 1 (less than 10 ppm). The two fuels differed also significantly for the distillation curve and for the aromatic content.

The two emulsions were produced using the two base fuels (Fuel 1 and Fuel 2) and an identical formulation (6% water and 2500 ppm of cetane improver); however, due to the production procedure, the final blends of the two emulsions differed for the actual values of the cetane improver and water content (see table 7).

Tab. 6 – Base fuels

Property	Unit	Fuel 1	Fuel 2
Density @ 15 C	kg/l	0.843	0.822
Sulphur Content	mg/kg	<10	38
CFPP	° C	- 12	- 10
Cetane Number		52.8	51.6
Distillation			
	10 % vol ° C	212	178
	50 % vol ° C	262	233
	90 % vol ° C	340	320
	95 % vol ° C	354	342
Total Aromatics	% v/v	30.0	25.9
Polyaromatics	% v/v	4.2	3.9

Tab. 7 - Emulsions

Property	Unit	Emulsion 1 (Fuel 1)	Emulsion 2 (Fuel 2)
Density @ 15 C	kg/l	0.852	0.832
CFPP	° C	- 16	- 16
Cetane Number		51.6	50.5
EEN(Cetane Improver)	mg/kg	3347	1830
Water	% w/w	5.6	6.2

6.1.3 Emission tests

The emission tests were carried out on a chassis dynamometer using the New European Driving Cycle (NEDC).

Regulated emissions (HC, CO, NO_x and Particulates) were measured following the legislative measuring procedures.

At least two back-to-back tests were carried out with each fuel on each vehicle.

For all the vehicles the test sequence was the following:

Test n.	1	2	3	4	5	6	7	8
	Fuel 1	Fuel 1	Fuel 2	Fuel 2	Emulsion 1	Emulsion 1	Emulsion 2	Emulsion 2

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 4.

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 as below:-

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

Table 4

Back to back acceptance criteria							
LD diesel	HC <0.05g/k m	HC >0.05g/k m	CO <0.10g/k m	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

6.1.4 Instrumentation details

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

Two different test cells were used to carry out the emission tests: the passenger cars were tested in the JRC's VELA 1 test cell while the van was tested in the VELA 2 test cell. The main characteristics of the two test cells are reported here below.

VELA 1 (Passenger cars)

The CVS is equipped with four critical orifices that allow to select the most appropriate flow rate from a minimum of 1.5 m³/min to a maximum of 11.25 m³/min.

The roller bench of the chassis dyno was a single roller type manufactured by Zoellner GmbH:

- Diameter: 48"
- Inertia range: 150-3500 kg
- Maximum speed: 200 km/h

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

Emission measurements were performed using the following analysers:

- **CO:** Hartmann & Braun IR analyser.
- **NOx:** Hartmann & Braun chemiluminescence analyser.
- **HC:** Hartmann & Braun 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.

VELA 2 (Van)

The CVS is equipped with four critical orifices that allow to select the most appropriate flow rate from a minimum of 3.1 m³/min to a maximum of 30.8 m³/min.

The roller bench of the chassis dyno was a single roller type manufactured by MAHA GmbH:

- Diameter: 48"
- Inertia range: 454 - 4500 kg
- Maximum speed: 200 km/h

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

Emission measurements were performed using the following analysers:

- **CO:** Horiba IR analyser.
- **NO_x:** Horiba chemiluminescence analyser.
- **HC:** Horiba 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.

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 were heated up at 50 °C with a heating jacket.

7 Results

7.1 Regulated Emissions - All Vehicles

Gaseous Emissions

Compared to the values obtained with the base fuels, all the vehicles exhibited higher HC emissions when they were fed with the emulsions (Fig. 13-15).

From a qualitative point of view, the effect of the emulsions on HC emissions was quite similar for all the vehicles and for the two base fuels. The percentage variation of HC emissions ranged from a minimum of +18% (vehicle VAN(M), Fuel 2) to a maximum of +49% (vehicle PC(F), Fuel 1).

Hydrocarbon emissions are currently regulated only together with NO_x emissions: in fact there is a limit only for the sum HC+NO_x. As the vehicles tested exhibited very low HC levels, the significant increase of HC emissions noticed had little impact on the sum NO_x+HC (Fig. 22); therefore the vehicles still met the emission limits when fed with the emulsions.

The use of the emulsions led to an increase of CO emissions on all the test vehicles (Fig. 16-18) as well; nevertheless, despite the higher emissions, the vehicles still met the emission standards for CO. The increase of CO emissions due to the emulsions was in general smaller than for HC emissions, ranging from +9% (vehicle PC(A), Fuel 2) to +35% (vehicle VAN(M), Fuel 2).

NO_x emissions (Fig. 19-21) showed a downward trend with the emulsions but in general the effects were very small. In the case of vehicle PC(F) and Fuel 1 an increase of NO_x emissions was noticed; however, the analysis of other test data demonstrated that it was an outlier result, probably due to a malfunctioning of the roller bench that did not simulate correctly the running resistance during part of the cycle.

Finally, the base fuel do not seem to play an important role in influencing the effect of the emulsions on gaseous emissions; from a qualitative point of view, the effect of the emulsions do not depend on the quality of the base fuel while the magnitude of the effect depends on it only to a limited extent.

Fig.13 –Vehicle PC(A): Hydrocarbon Emissions

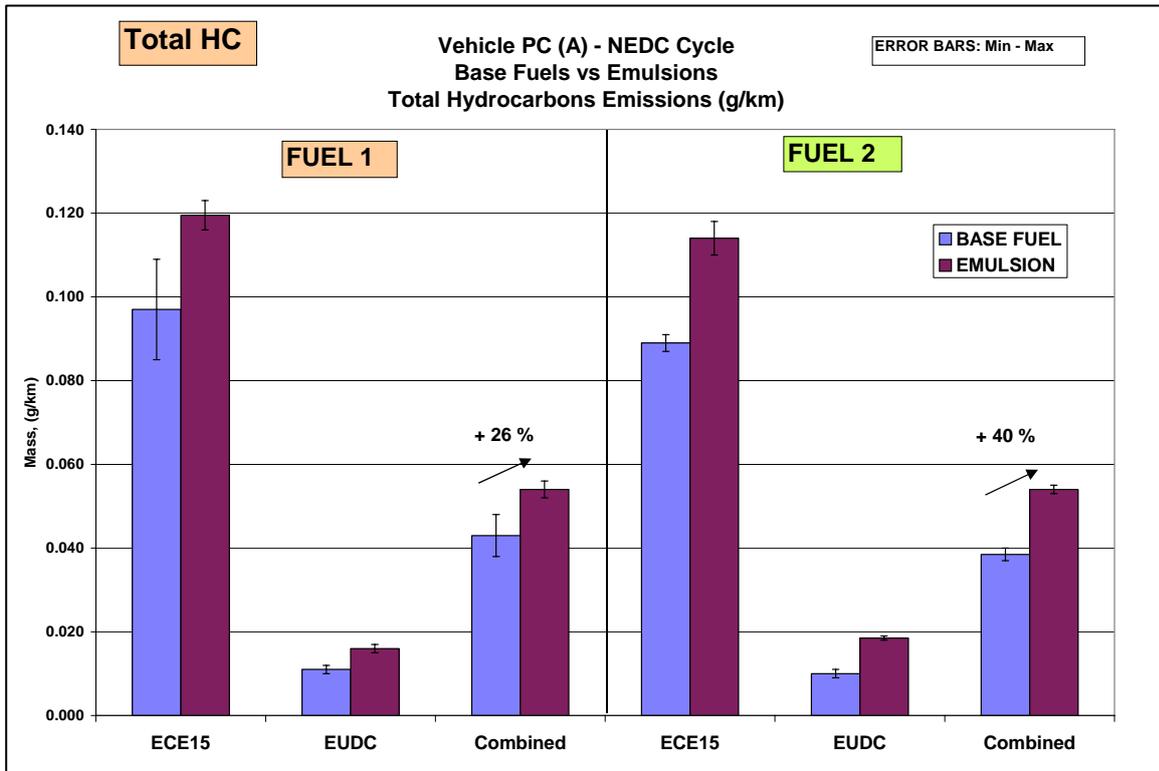


Fig. 14 –Vehicle PC(F): Hydrocarbon Emissions

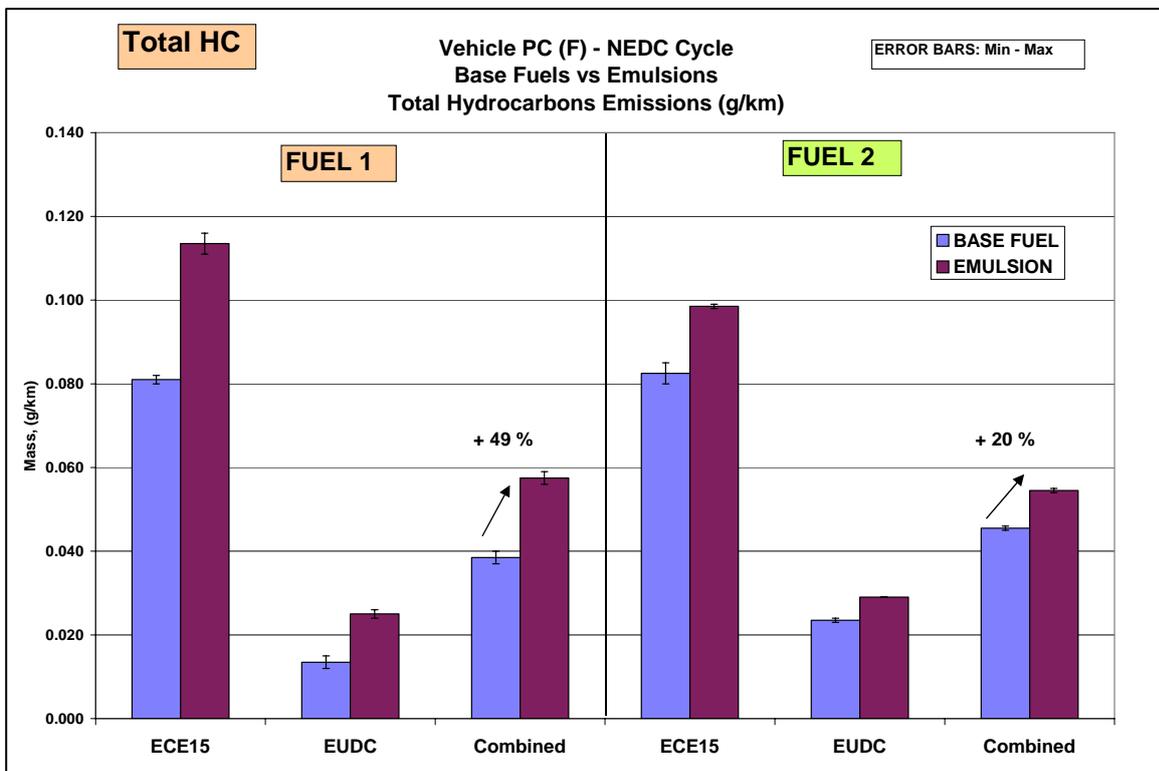


Fig.15 –Vehicle VAN (M): Hydrocarbon Emissions

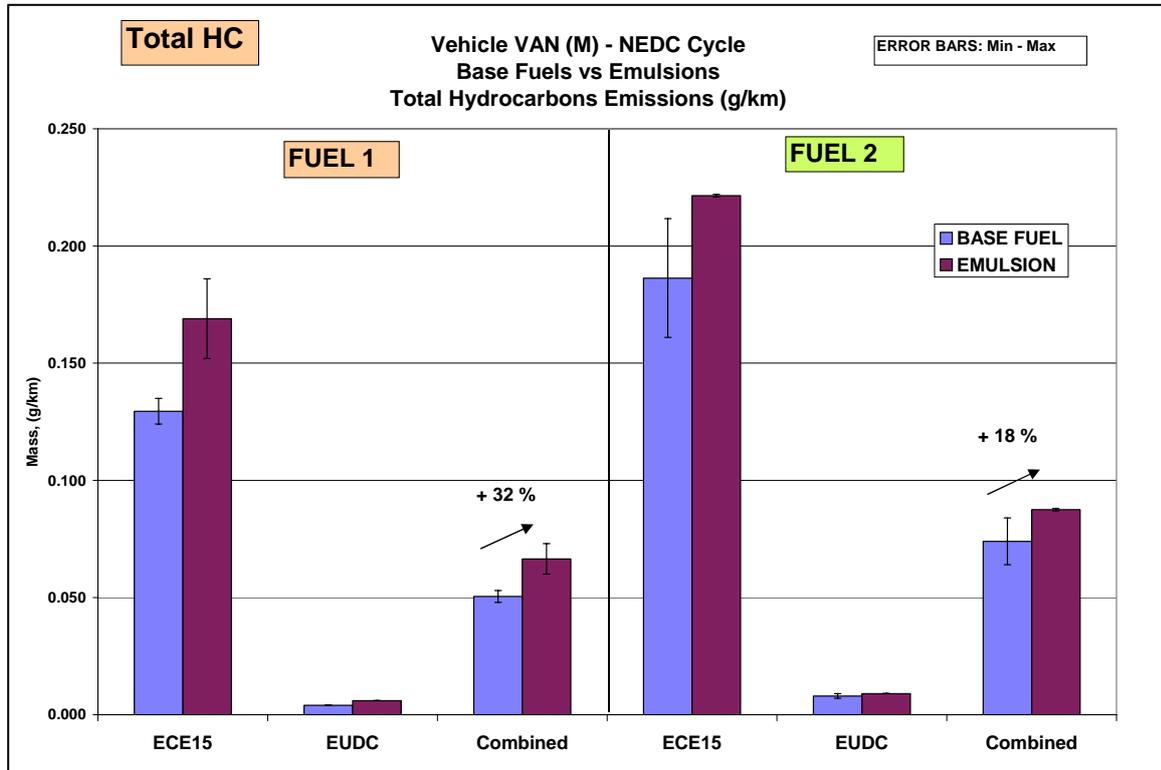


Fig. 16 –Vehicle PC(A): CO Emissions

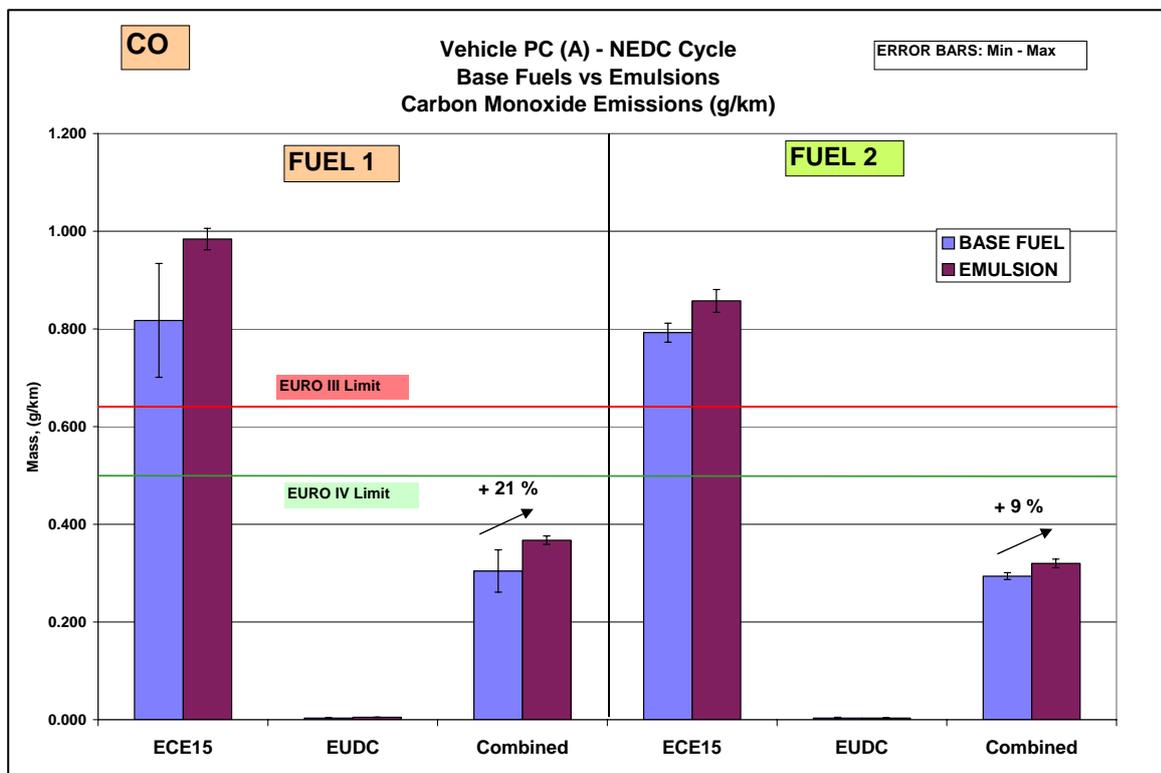


Fig. 17 –Vehicle PC(F): CO Emissions

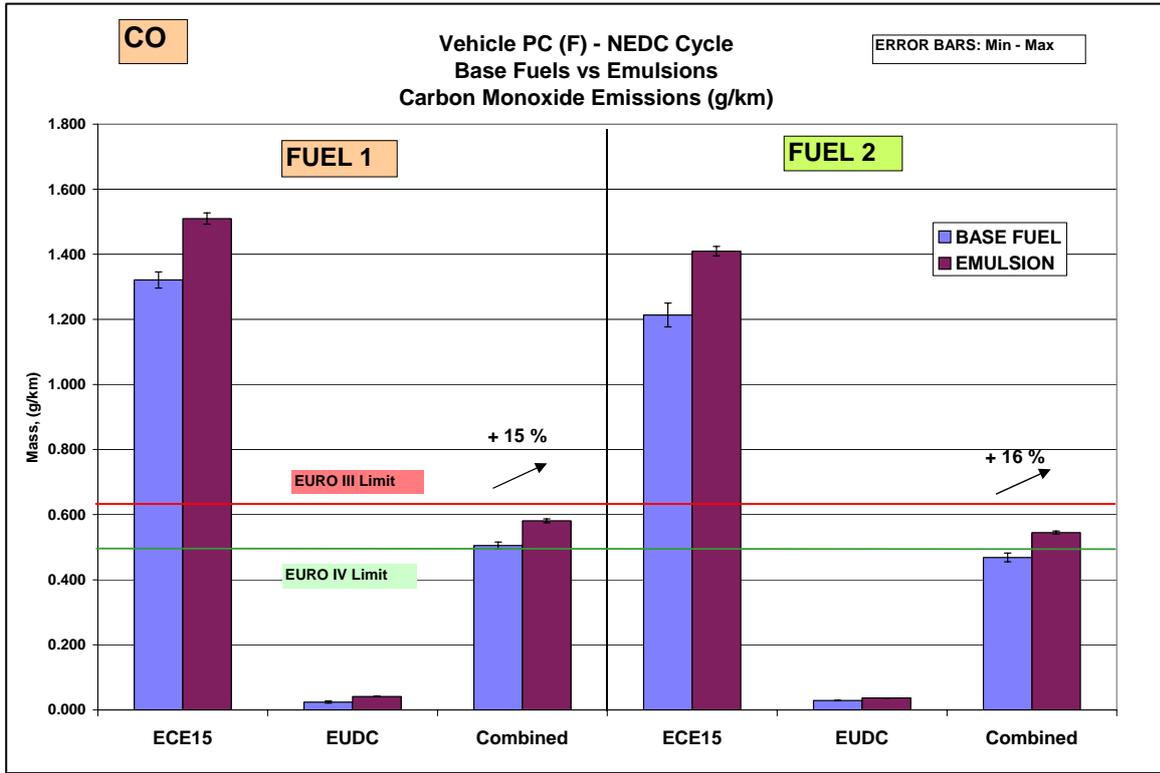


Fig. 18 –Vehicle VAN(M): CO Emissions

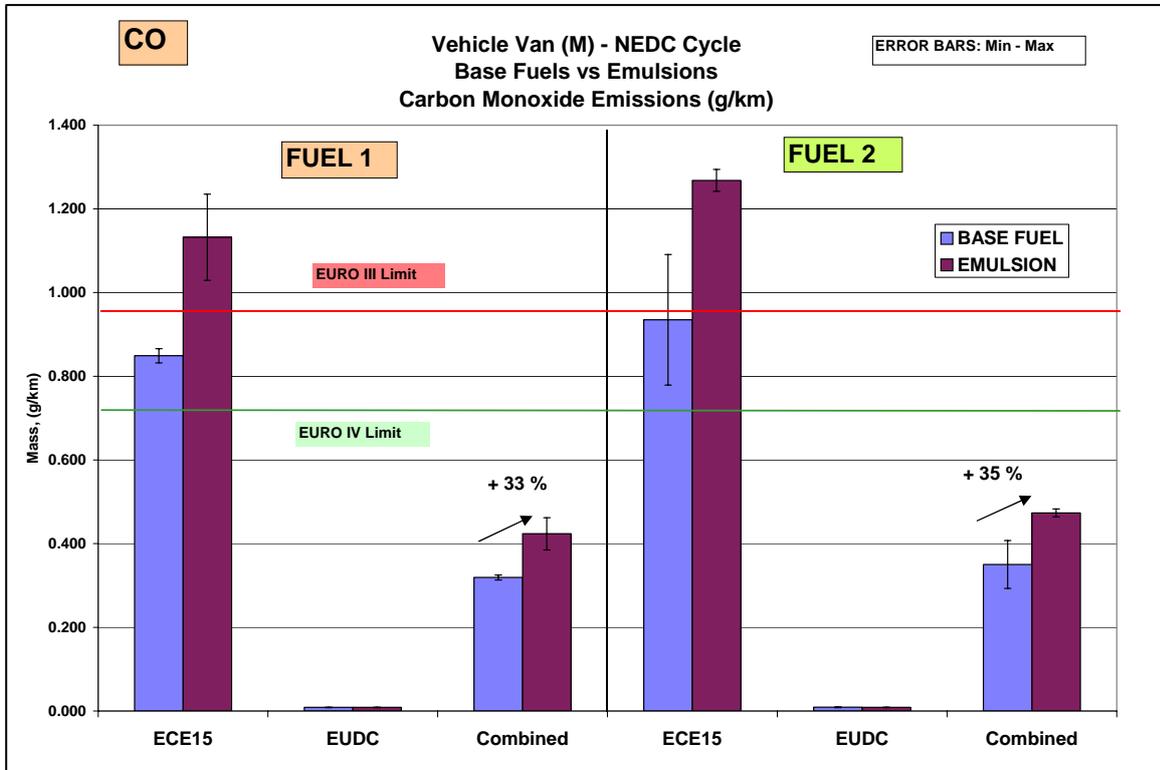


Fig. 19 –Vehicle PC(A): NOx Emissions

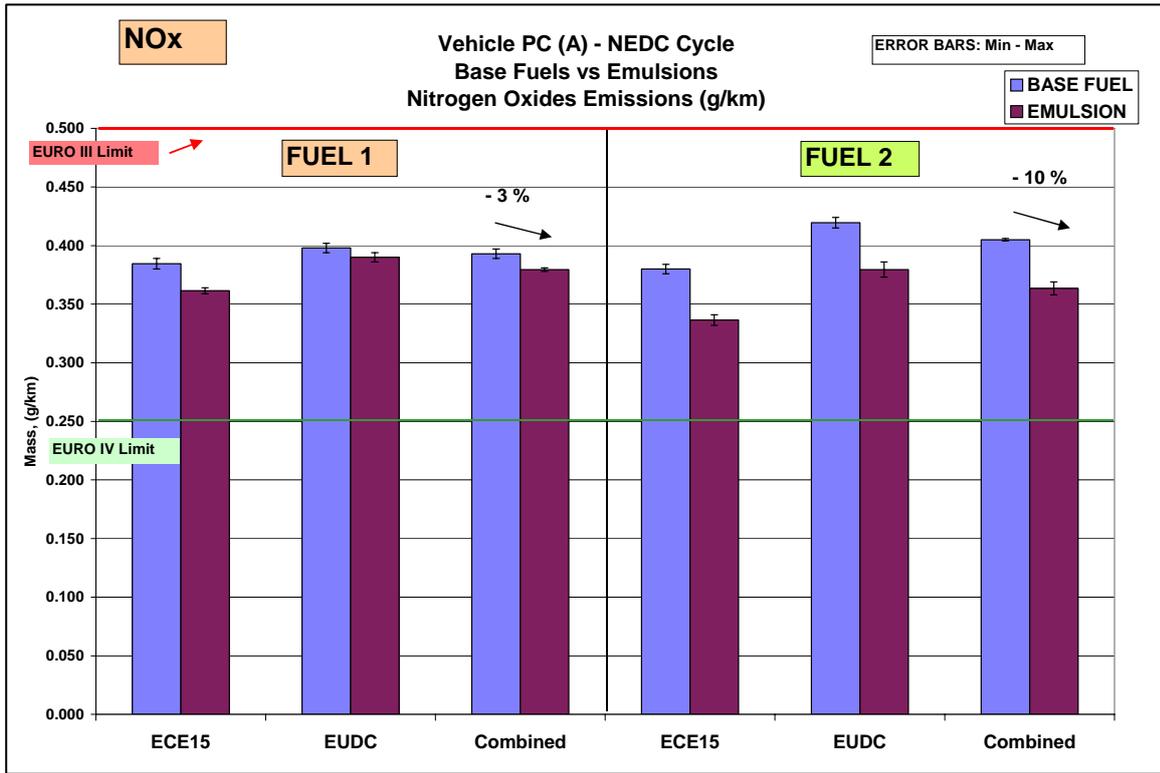


Fig. 20 –Vehicle PC(F): NOx Emissions

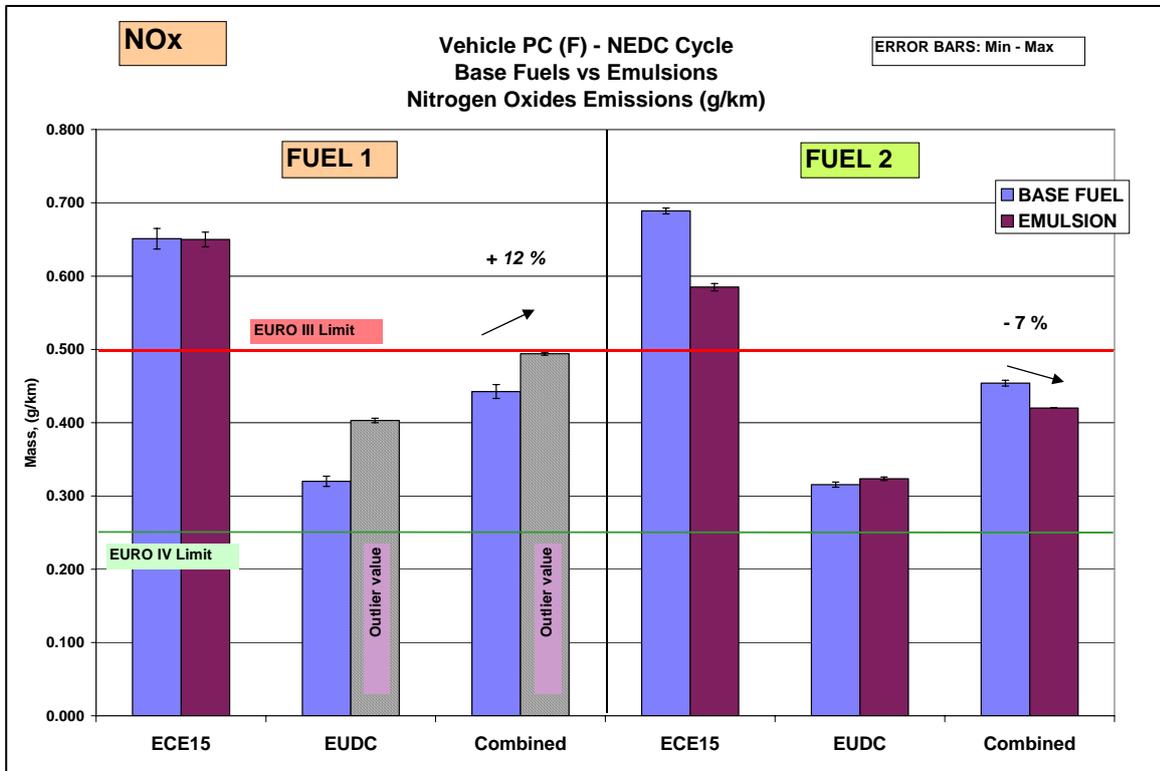


Fig. 21 – Vehicle VAN(M): NOx Emissions

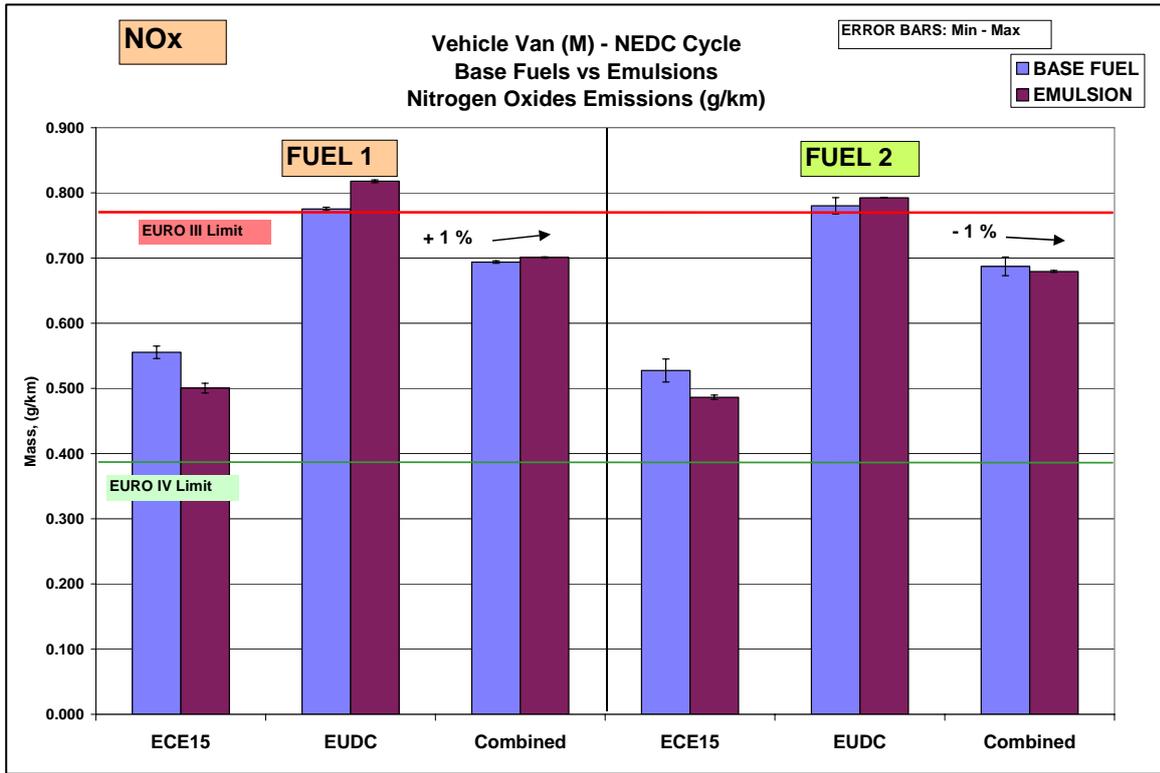
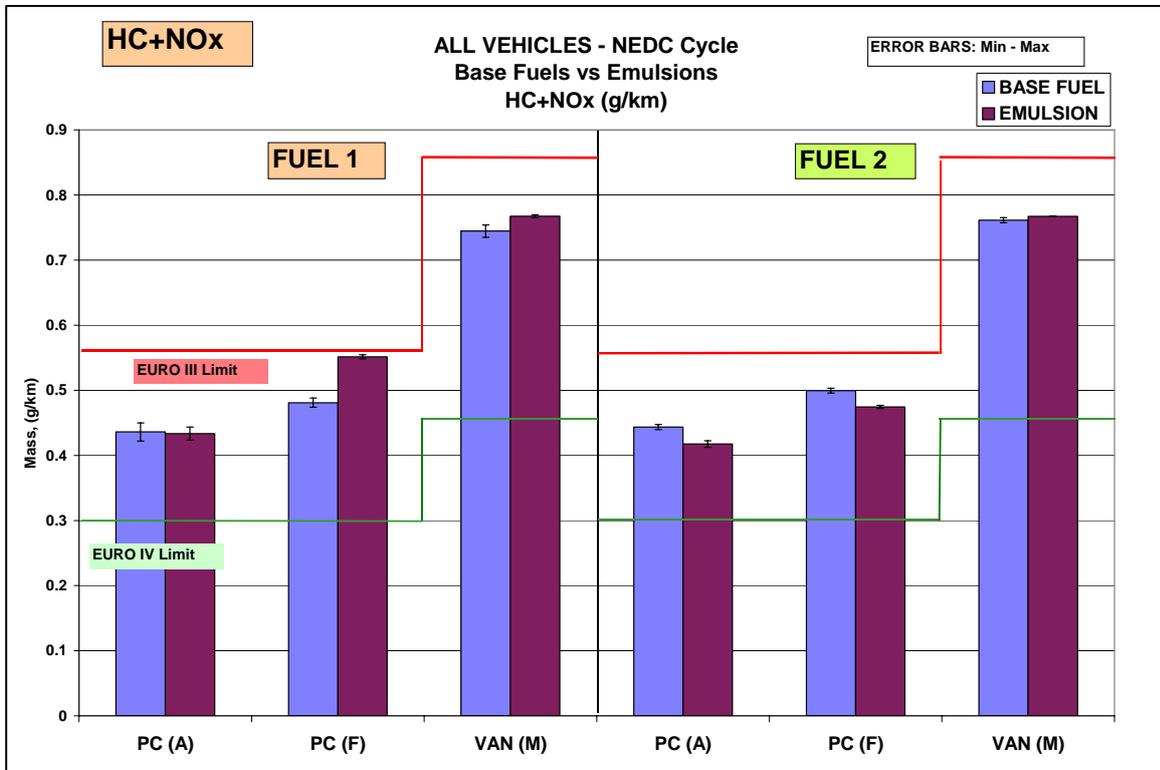


Fig. 22 – All vehicles: HC+NOx



Particulate emissions

As far as particulate emissions are concerned, the effect of the emulsions was very evident: an important reduction of PM emissions in terms of total mass was noticed on all the vehicles (Fig. 23-25). The minimum percentage variation was -31% (vehicle PC(A), Fuel 1) while the maximum value was -45% (vehicle VAN(M), Fuel 2).

Moreover, the reduction of particulate emissions was similar for both the urban (ECE 15) and the extra-urban part of the cycle (EUDC).

Concerning the influence of the quality of the base fuel, the plots show that although the base fuel Fuel 2 gave lower PM emissions, the effect of the emulsions was a bit larger than in the case of Fuel 1.

Fig. 23 –Vehicle PC(A): PM Emissions

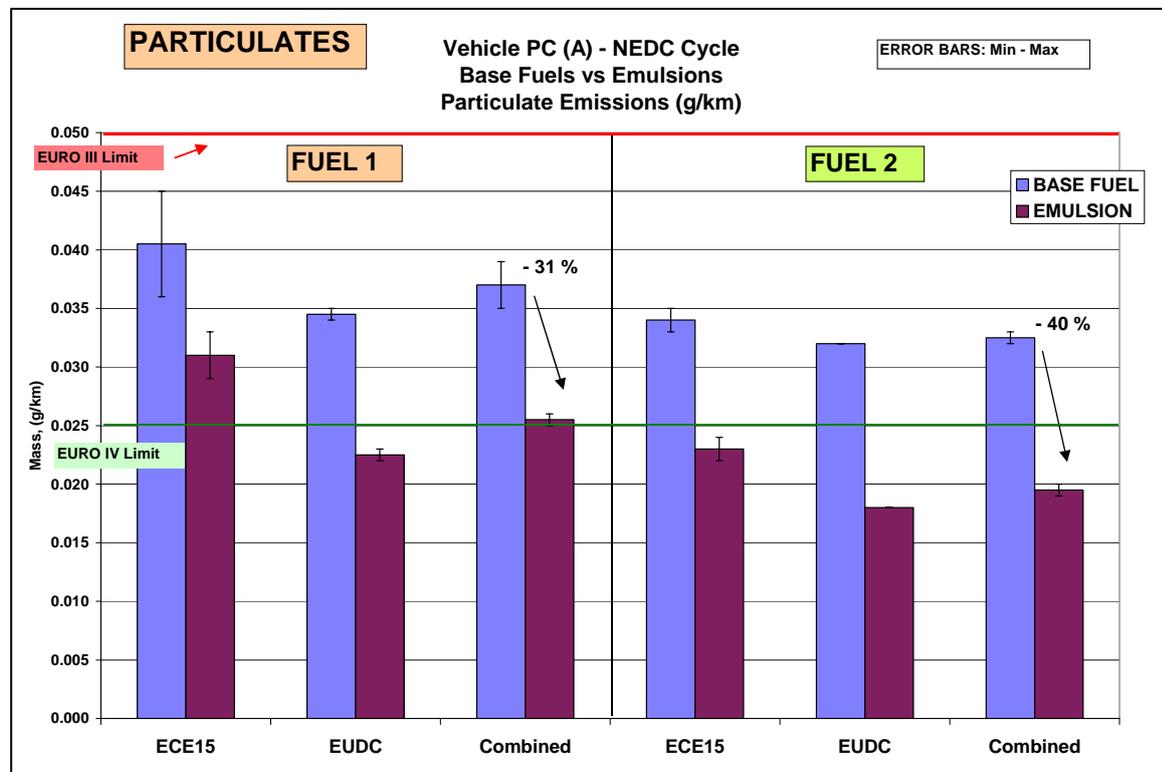


Fig. 24 –Vehicle PC(F): PM Emissions

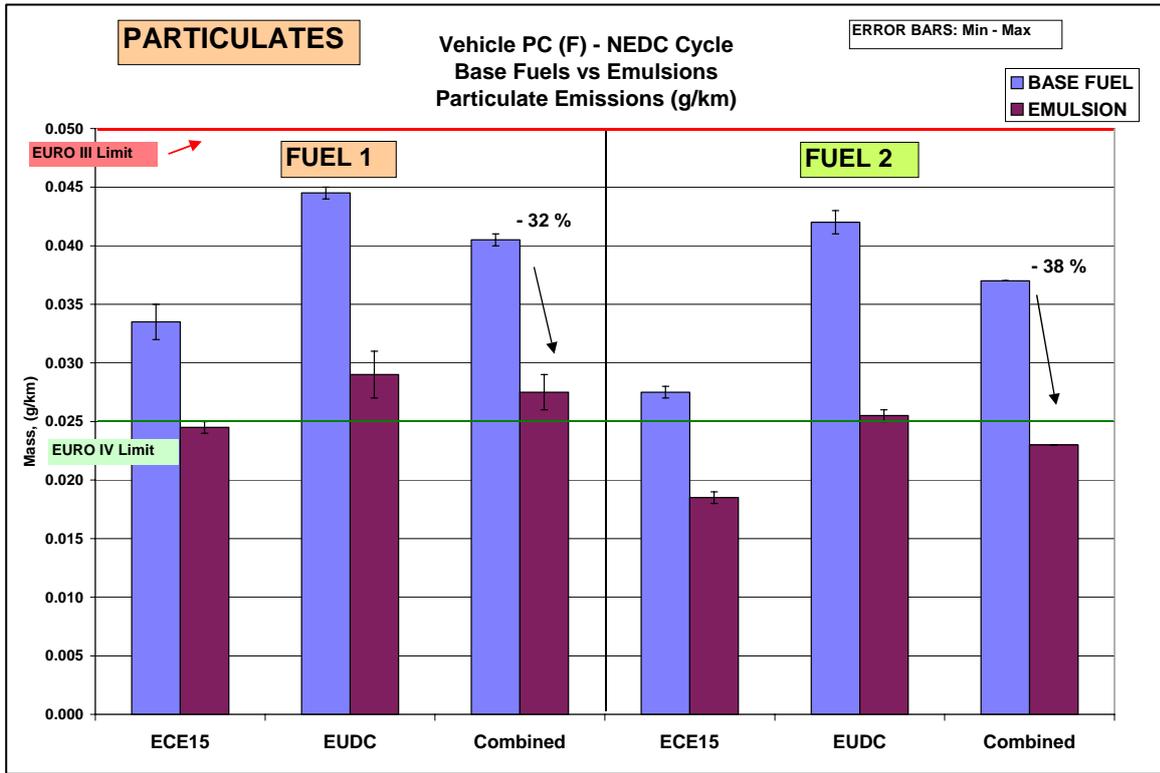
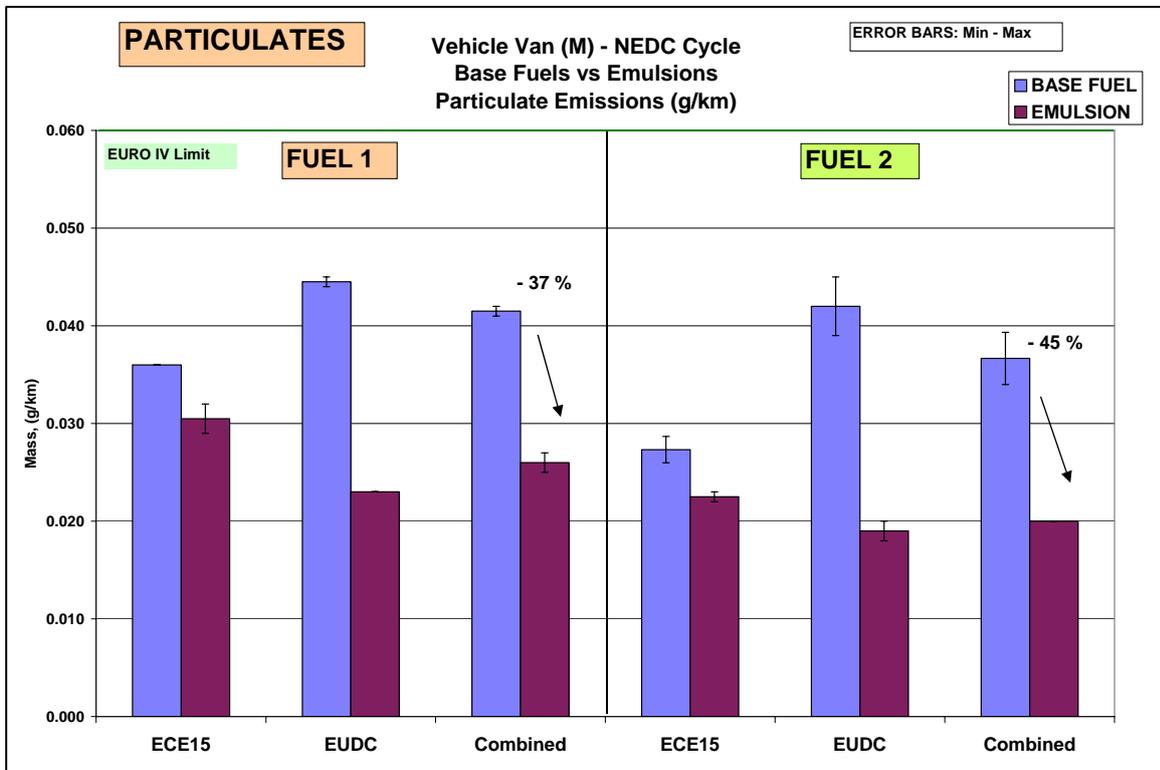


Fig. 25 –Vehicle VAN(M): PM Emissions



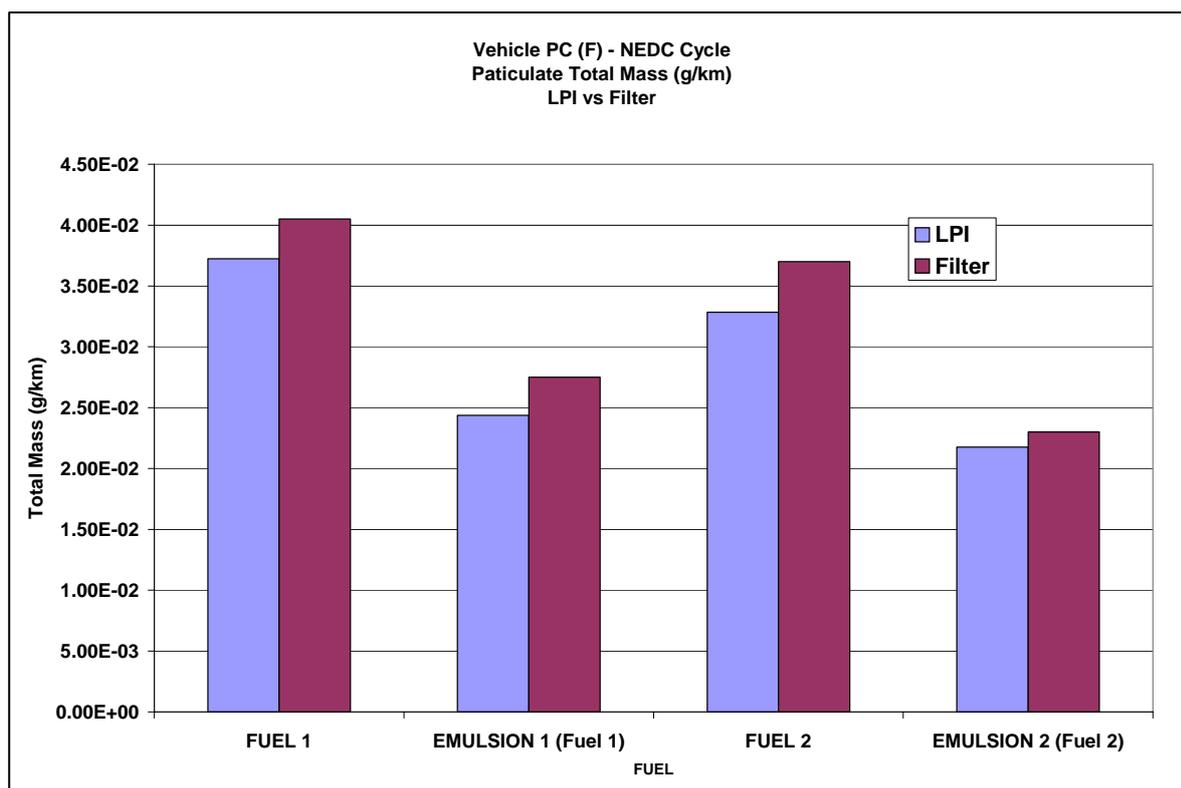
7.2 Mass/Size Distribution

The mass/size distributions of particles emitted by the test vehicles were measured by means of a Low Pressure Impactor (LPI); the distributions obtained with the base fuels were then compared with the distributions obtained with the corresponding emulsions.

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

First of all, the mass/size distributions resulted to be in very good agreement with the total mass measured using the filter method. As an example (passenger car F), in the figure 26 the total mass measured with the filter and the one calculated adding up the mass collected on each stage of the impactor are compared. Despite the total mass obtained with the LPI is always a bit lower than the mass measured according to the legislative procedure (probably due to a different deposition efficiency and to a loss of volatile material in the LPI because of the low pressure), the ranking of the test fuels, with respect to the emission levels, is exactly the same.

Fig. 26 – Comparison between the total mass measured with the filter and the LPI



Furthermore, 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. In other words, the mass/size distribution shape did not change significantly changing the fuel from the normal ones to the emulsions.

Fig.27 –Vehicle PC(A): Particulate Mass/Size Distribution

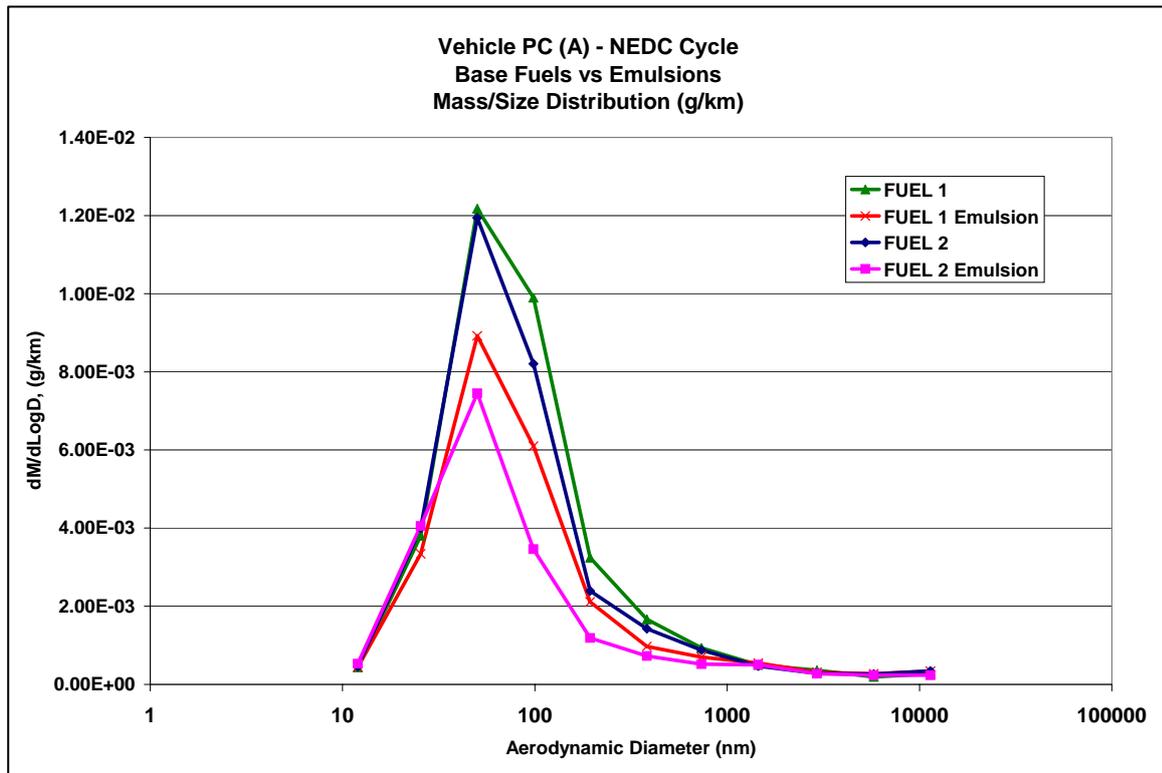


Fig. 28 –Vehicle PC(F): Particulate Mass/Size Distribution

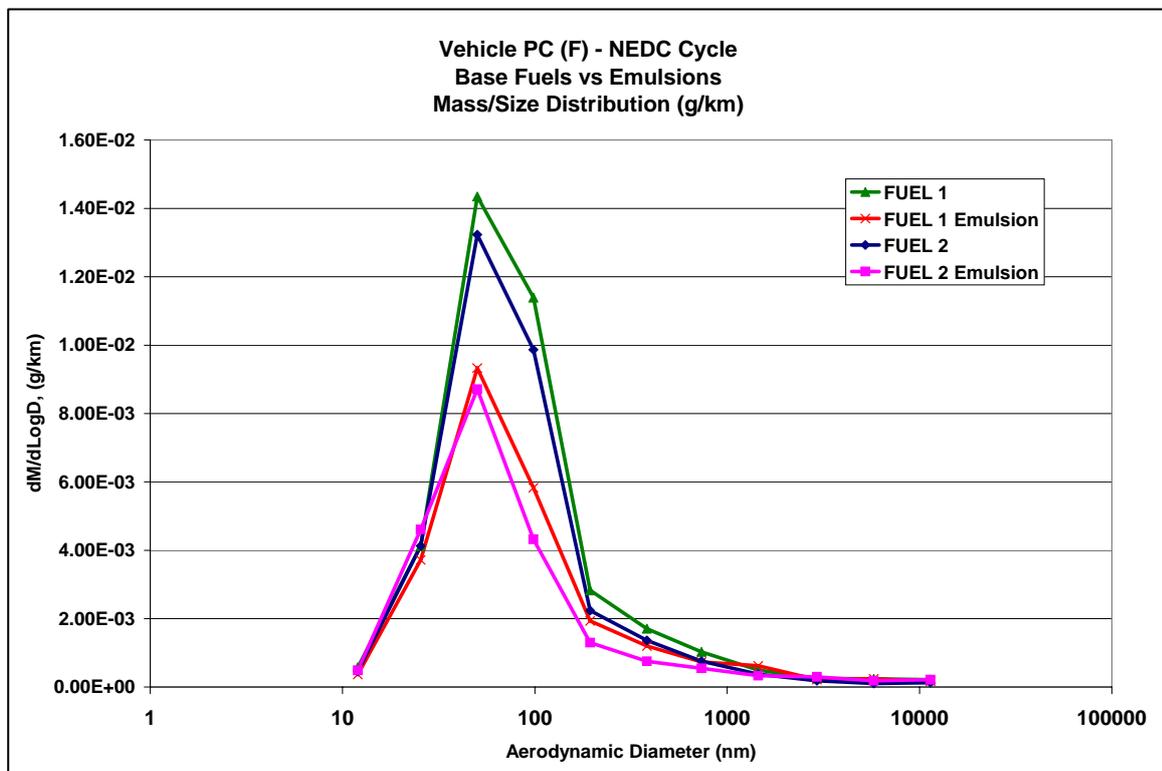
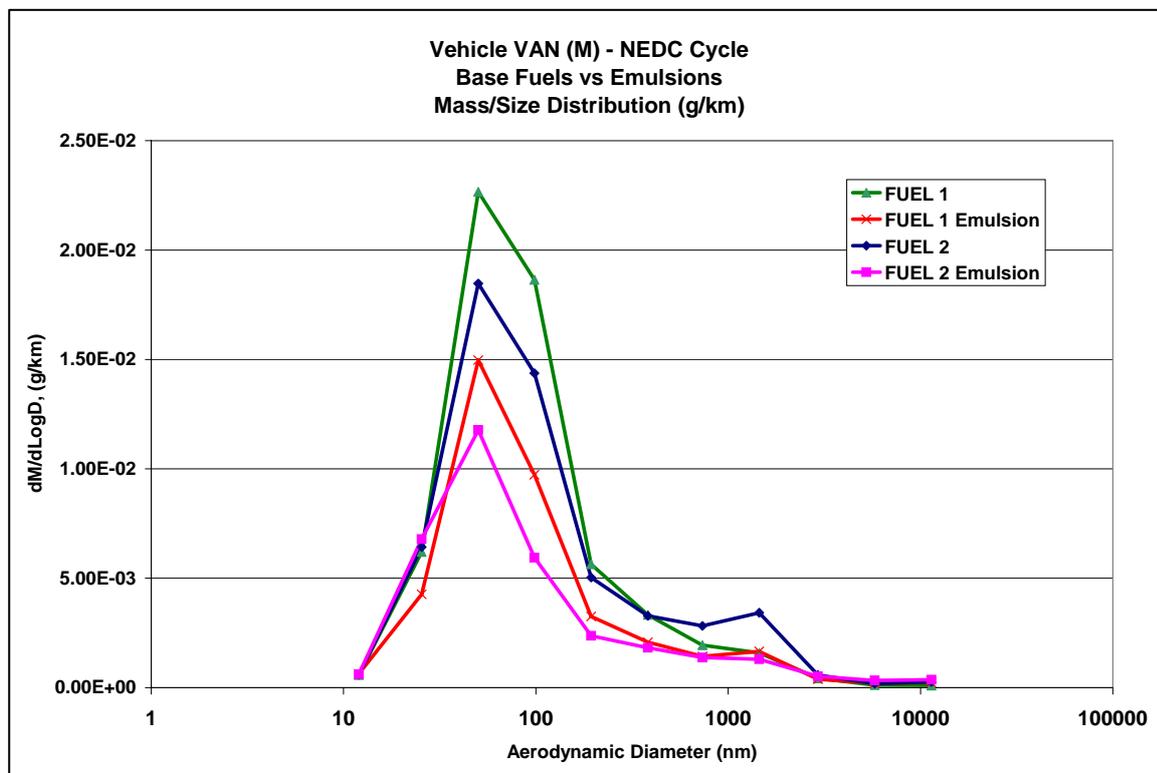


Fig. 29 –Vehicle VAN(M): Particulate Mass/Size Distribution



7.3 Exhaust temperature

During the emissions tests the temperature of the exhaust gas at the outlet of the tailpipe was recorded continuously by means of a thermocouple.

The temperature profile for each vehicle and for each fuel is shown in the figures 30-32 (in the case of the light commercial vehicle, only the temperatures measured with the Fuel 2 are reported).

The plots show clearly that the exhaust temperature profile was very similar for all the fuels; therefore the emulsions should not have affected the light-off time and the efficiency of the oxidation catalyst. As a consequence, the differences in CO and HC emission noticed between the diesel fuels and the emulsions cannot be ascribed to a lower catalyst efficiency but mainly to higher engine out emissions..

In the case of the vehicle PC (F) the exhaust temperature profiles can also explain why the tests performed with the Emulsion 1 gave higher NO_x emissions. In fact, over the EUDC part of the cycle, the exhaust temperature was higher with Emulsion 1 than with the other fuels; that could be due to the roller bench not correctly operating: in particular, a higher running resistance could

have been applied during that part of the cycle as demonstrated also by the higher CO2 emissions.

Fig. 30 –Vehicle PC(A): Exhaust gas temperature (Post-Cat)

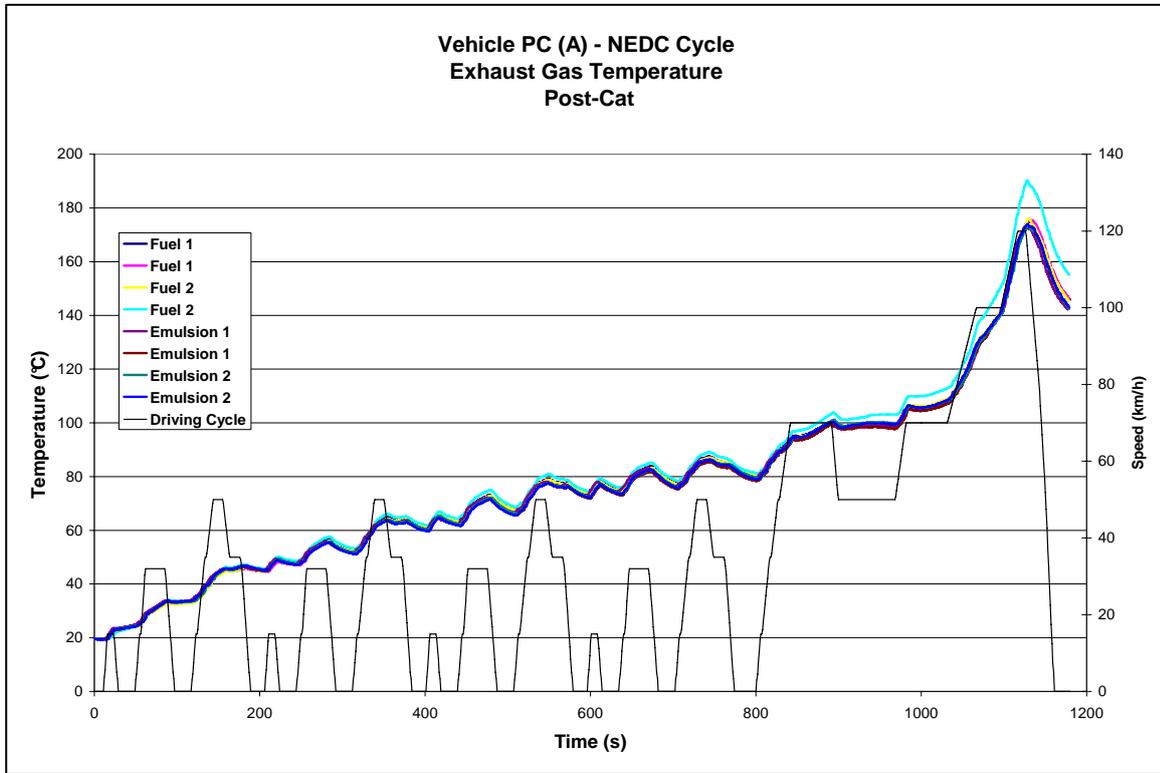


Fig. 31 –Vehicle PC(F): Exhaust gas temperature (Post-Cat)

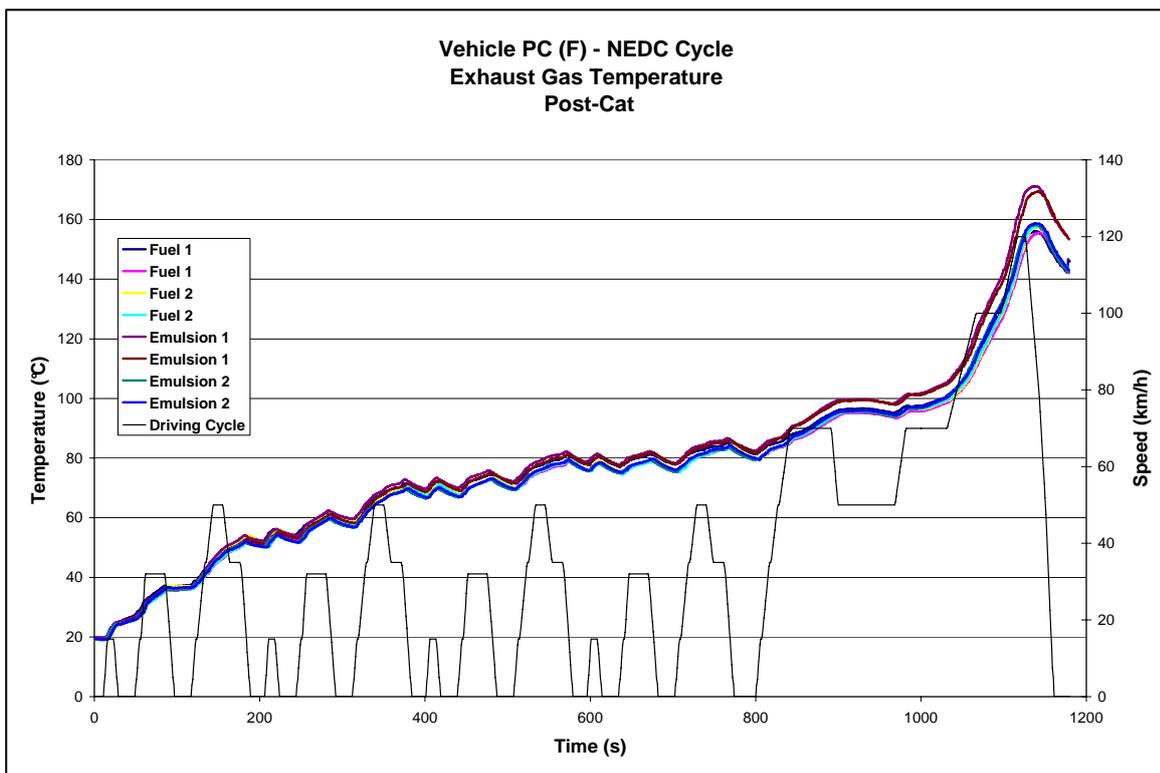
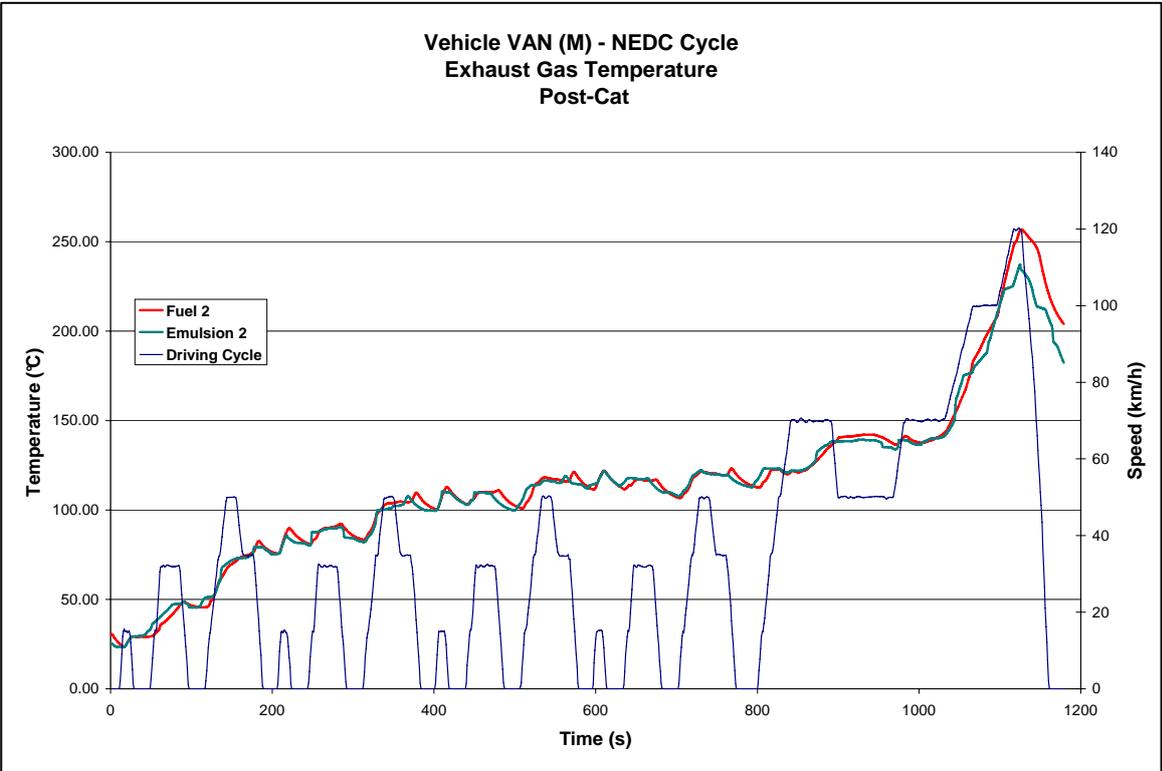


Fig. 32 –Vehicle VAN (M): Exhaust gas temperature (Post-Cat)



7.4 Unregulated emissions: Chemical composition of particulates

Same way as we did in the preceding chapter for a HD engine, we will see now what happens to unregulated emissions coming from three different LD vehicles when we fill them alternatively with a reference diesel fuel or with a 6% water/diesel (W/D) emulsion.

In the previous pages we conclude that using 12% W/D emulsion in a HD vehicle leads to a benefit not only by decreasing the amount of PM emitted but also by improving the quality of this particulate. In this section we will have the opportunity to see how different behaves a LD engine loaded with 6% W/D emulsion. Under these conditions there is no benefit anymore that justifies the use of the emulsion instead of the reference fuel. Indeed, the use of commercial W/D emulsions containing 6% water in LD diesel vehicles only reduced significantly the emissions of PM (-32%) but clearly increased emissions of Hydrocarbons (+26%), CO (+18%) and the Toxicity equivalent of the mixture, TEQ (+25%).

For these experiments, three EURO 3 vehicles with similar characteristics were considered: two cars and a “Van” type LD vehicle. The main difference between the two cars, from the technological point of view, is that the first one is equipped with Unit Injector technology while the second one uses Common Rail technology.

The sampling, clean up and analysis of the exhaust were done following the same protocol described in section 4.3. Two commercial diesel fuels and their corresponding emulsions with 6% water on it were considered (see tables 6-7). Some of the main differences between the two reference fuels are density and content in aromatics. Both characteristics will play an active role in the results that we will analysed following.

Regarding their PAHs content of the exhaust, vehicle PC (A), performs a little bit worse than vehicle PC (F) (see Fig. 33-34). If we compare the two different emulsions we can observe that vehicle A performs a little bit better when emulsion prepared with Fuel 2 is used. This result could be due to the fact that density of fuel 2 is lower than Fuel 1.

When we tested the second vehicle, F, we detected a slight decrease of the total amount of PAHs in both cycles when the emulsion was tested. No difference between Fuel 1 and 2 could be remarked when using this car

The third vehicle, VAN (M), considered in this study belongs to a different category (large passenger car with more than 6 seats) so it has to be considered individually and it should not be compared with the two previous ones. In any case the vehicle tested showed a very light decrease in the amount of PAHs in both cycles and for both emulsions but not significant enough to be considered as an alternative.

In conclusion the effect of emulsions on the PAHs content of the PM emissions from Light Duty vehicles is quite the same for all the vehicles considered in this study independently of the base fuel used for the experiments. Even though we may remark that the fuel 2 which has lower density behaves slightly better than Fuel 1, either when it is alone or when we use it as W/D emulsion. It remains also quite clear that this is not a feasible solution to reduce the potentially hazardous compounds emitted by LD vehicles as it was for HD.

Fig. 33

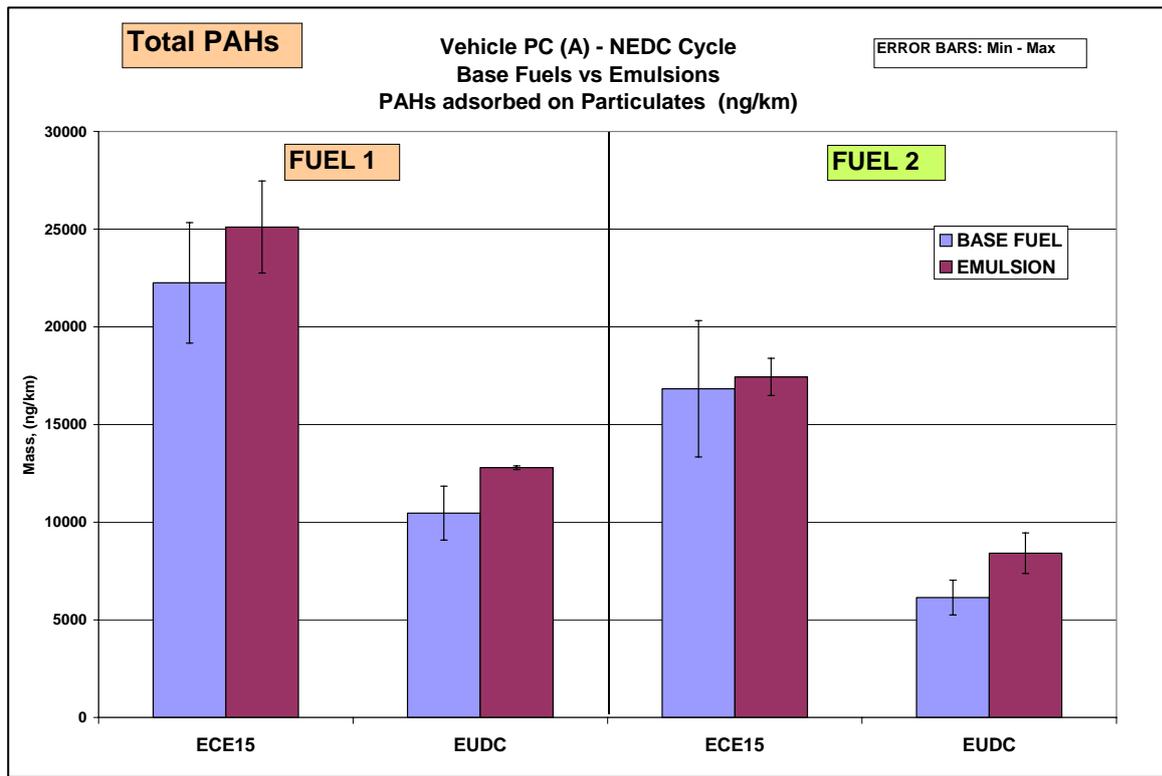


Fig. 34

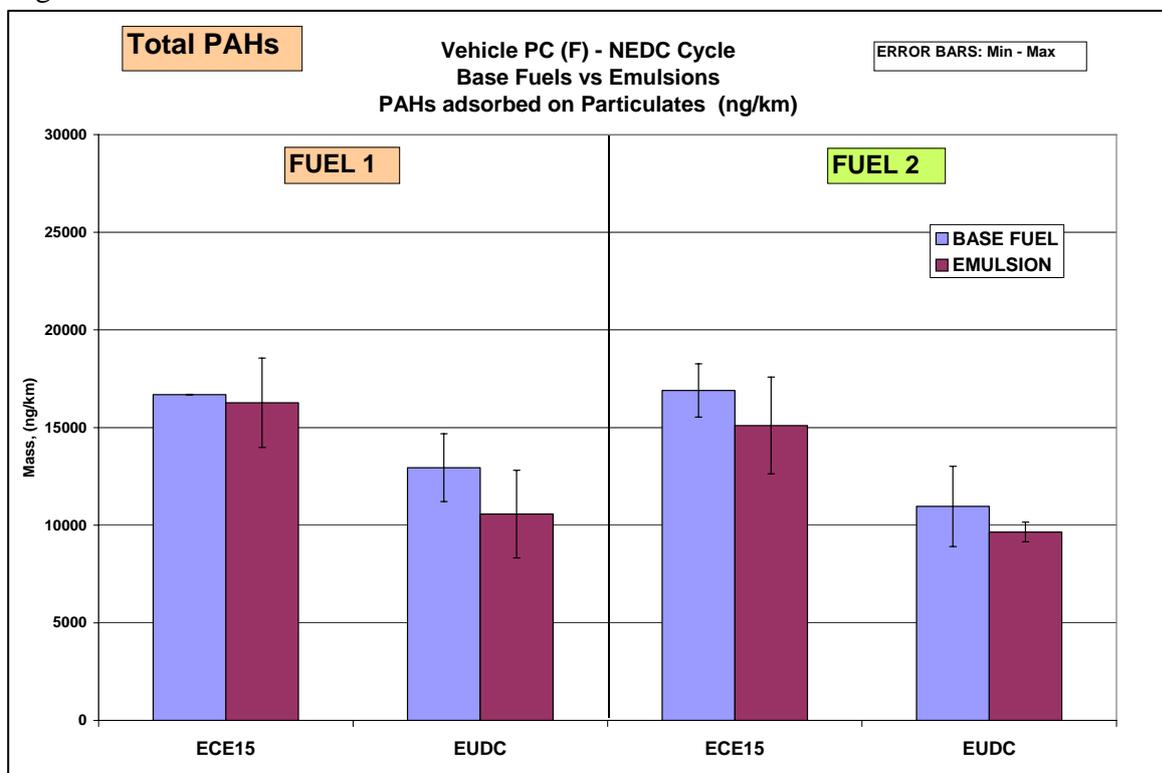
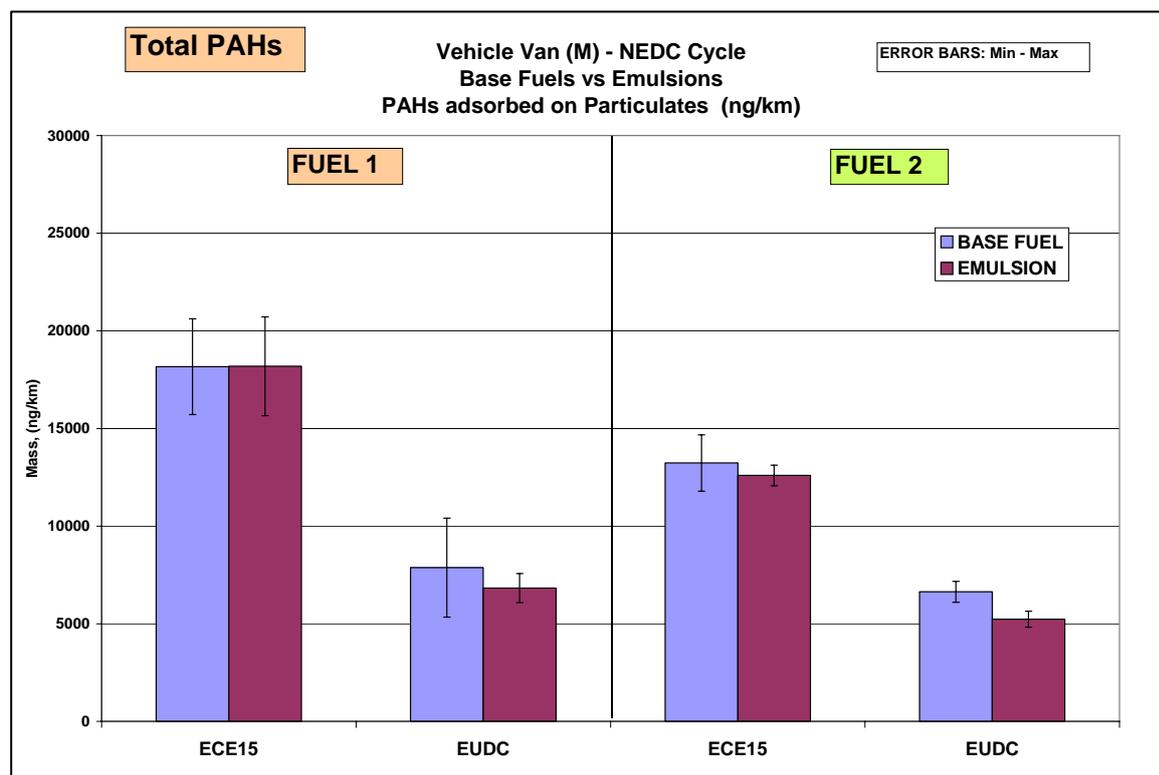


Fig. 35



7.4.1. Overall potential toxicity of the Mixture

To enable the relative potential toxicity of such a mixture of compounds to be expressed as a single number, the concept of toxic equivalents (TEQ) has been applied (More information in section 4.3.2). The overall toxicity or toxic Equivalents (TEQs) of a Mixture are defined by the concentration of individual compounds (C_i) in a mixture times their relative potencies or TEFs

$$TEQ = \sum [C_i] \times TEF_i$$

We have applied this approach to the PAHs results showed previously for the three different LD vehicles. We could observe that in all cases the values of TEQ obtained when using the emulsions, either the one from fuel 1 or from fuel 2, are slightly higher than the ones obtained with the reference fuel. That means that the use of 6% W/D emulsions in light duty passenger cars has not a positive influence in the quality of the emissions in terms of toxicity.

Fig. 36

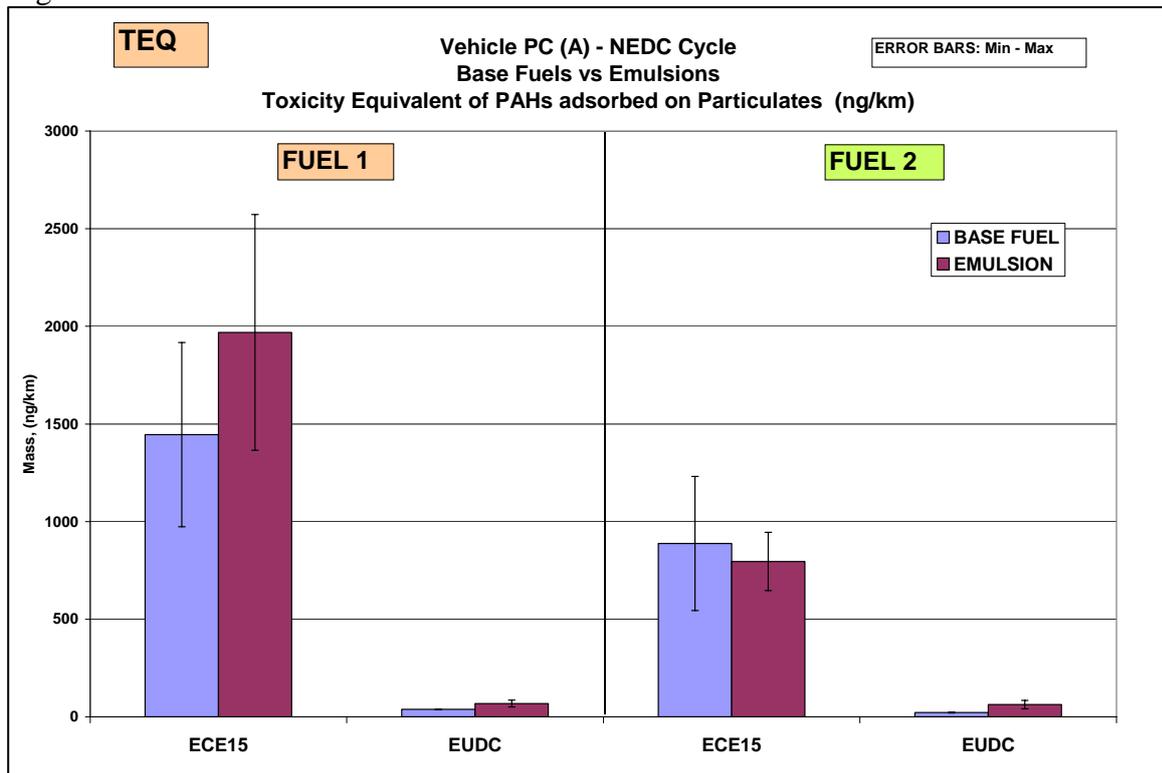


Fig. 37

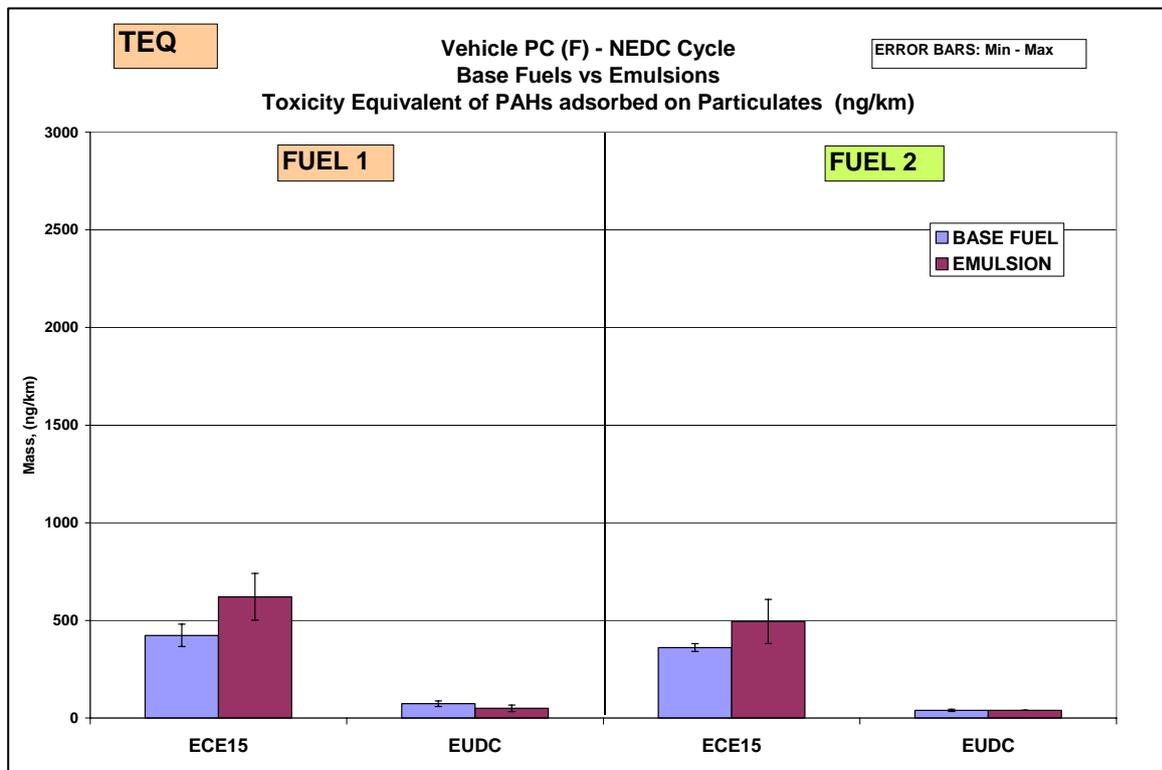
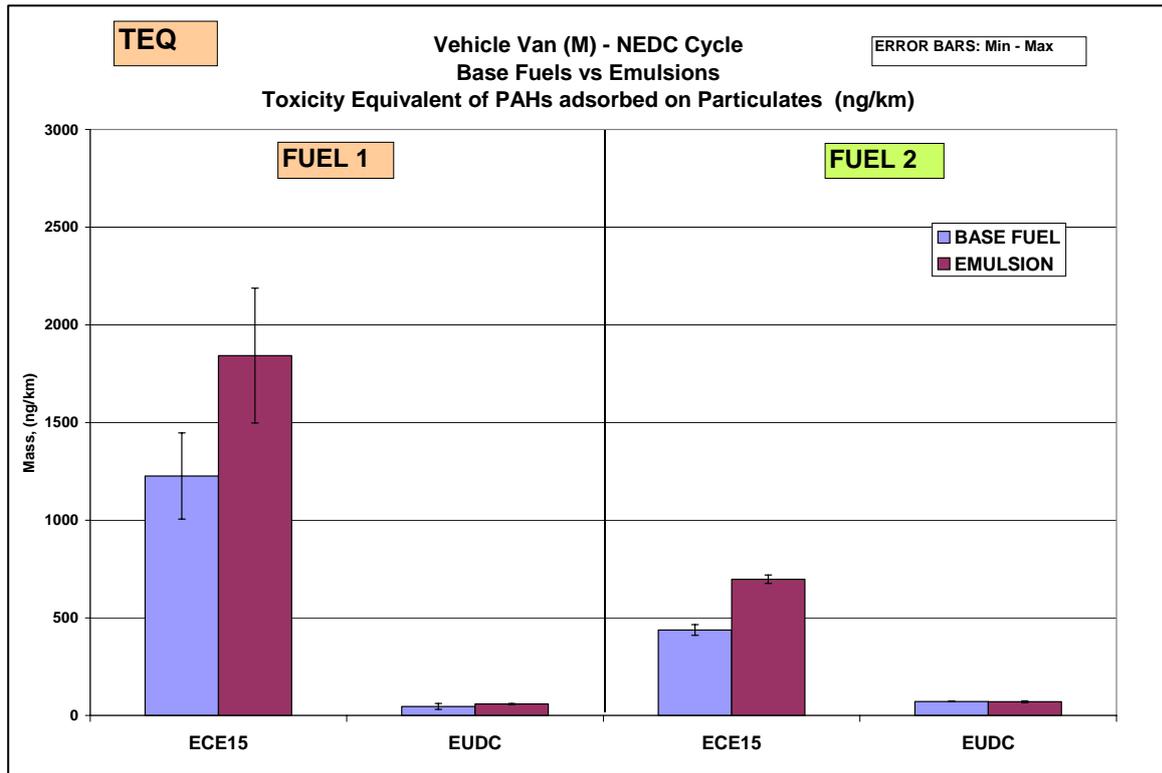


Fig. 38



7.5 Speciation of Volatile Organic Compounds (VOCs)

Since ground-level ozone is one of the air pollutants of most concern in Europe, a current subject is the determination of the C₂-C₉ 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 as of 9 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.

For the present study we have performed vehicle emission measurements of 30 individual C₂-C₉ 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:

$$\text{MIR}_i = \max \{ d[\text{O}_3]_p / dE_i \}$$

Where [O₃]_p is the peak ozone formation and "E_i" is the emission of the VOC_i

Once we have calculated the MIR values we can use it to calculate the **Potential ozone formation** of an exhaust emission by using the following equation:

$$PO_3(\text{g/km}) = \sum i \{ \text{MIR}_i (\text{g O}_3/\text{g VOC}) E_i(\text{g/km}) \}$$

To carry out this part of the study passenger cars were driven on a chassis dynamometer (Zoellner GmbH) with a constant volume sampler (flow 7.5 m³/min). Ten liters of vehicle 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 was 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 a W/D emulsion to the 30 ozone precursors hydrocarbons in the air we conducted a number of emission measurements from the 3 LD vehicles we considered before.

7.5.1. Volatile organic Compounds in vehicle exhaust and their contribution to Ozone formation

If we have in mind the previous results for the Total Hydrocarbons values that have been showed in this chapter when talking about the regulated emissions we may expect also an increase in the amount of VOCs. Indeed, when quantified separately (see fig 40) we can observe, in all LD vehicles considered in this study, that the amount of VOCs present in the exhaust coming from W/D emulsions is always higher if compared to the reference fuels.

The relative contribution of each individual VOC to the potential ozone formation, estimated by the Maximum Incremental Reactivity (MIR) Approach. (see fig. 41) showed also a negative influence of the emulsion by increasing in all tests the potential of the mixture to create ozone.

Fig. 40

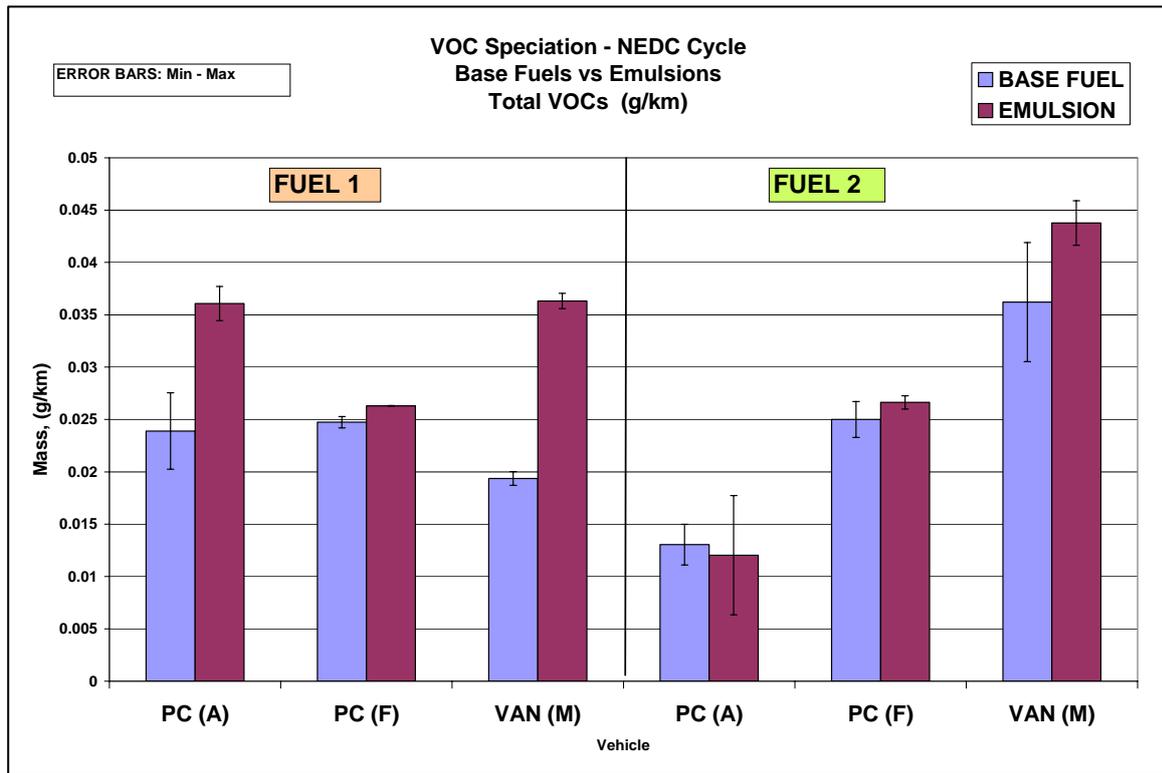
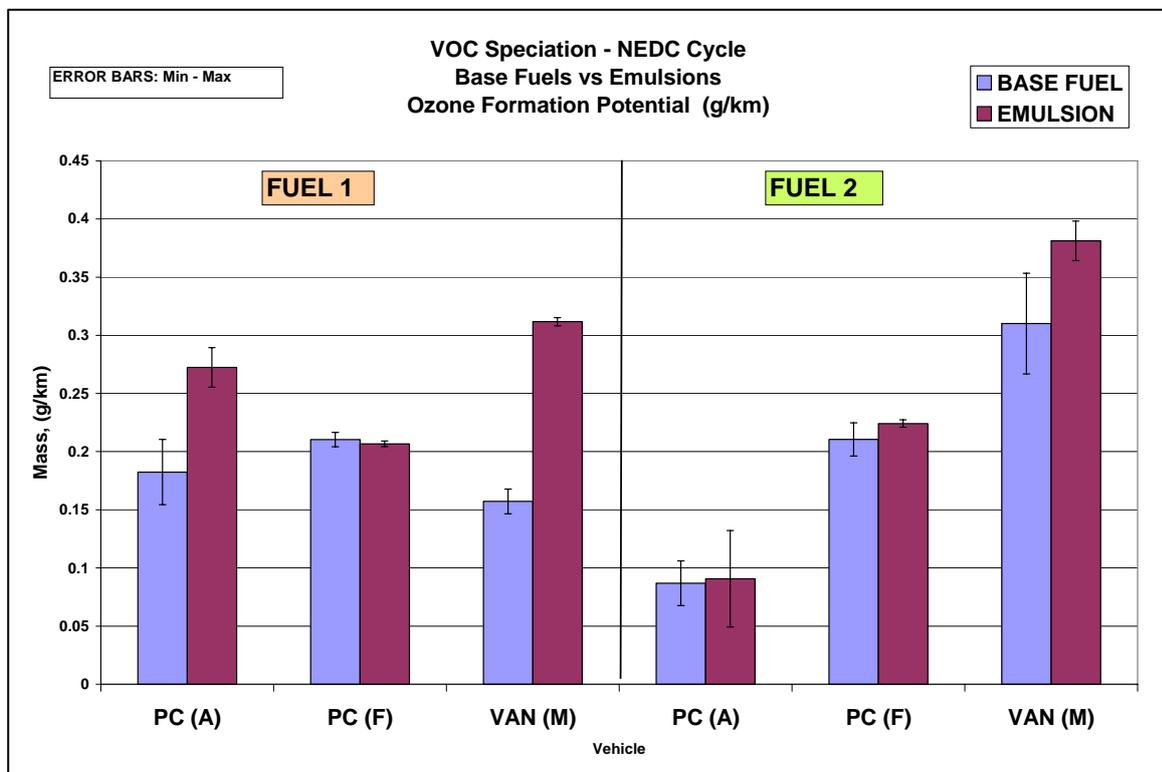
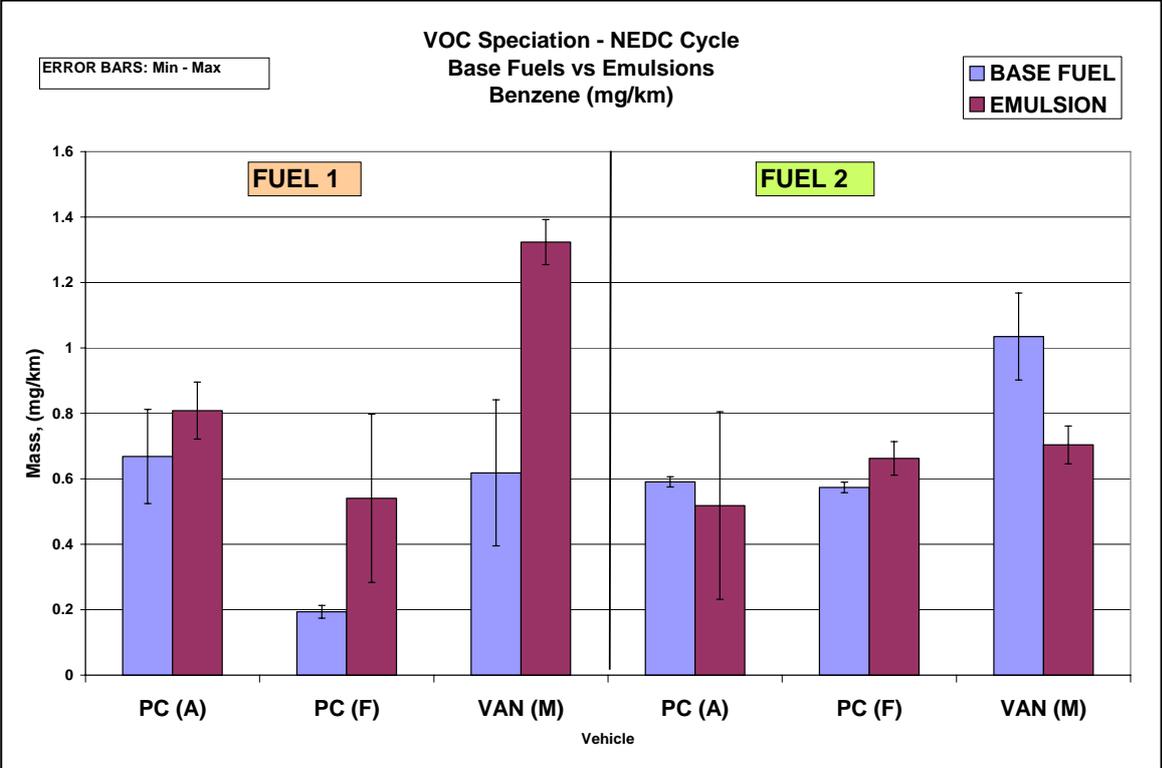


Fig. 41



Regarding the benzene content the Fuel 2 behaves a little bit better if we compared its results with those obtained with fuel 1. We may have an explanation to this fact in the description of the fuels (table 6-7). In fact the total content on aromatics for fuel 1 is 30% v/v while fuel 2 is only 25.9 % v/v.

Fig. 42



8 Conclusions

An experimental programme was carried out at the vehicle emission laboratory (VELA) of the JRC to investigate the effect of water/diesel fuel emulsion specially formulated for passenger cars.

The experimental programme consisted in emission tests carried out on three different diesel vehicles (two passenger cars and one light commercial vehicle) according to the current legislative procedure.

Four different fuels were tested: two commercial diesel fuels and two diesel/water emulsions. The two diesel fuels, used as base fuels, differed for density, distillation curve, aromatic content and other properties; the same diesel fuels were also used to produce the two test emulsions. The emission tests were initially carried out with the two diesel fuels to establish the base line of emission levels; then the tests were repeated using the two emulsions and the results were compared with those obtained with the related base fuel.

The main findings can be summarized as follows:

- In all the test vehicles, the diesel/water emulsions led to a significant increase of CO and HC emissions; the increase of CO emission was smaller than for HC emissions. Anyway it should be reminded that CO and HC emissions are not critical for diesel vehicles and emission levels are usually well below the emission standards; in fact, despite the significant increase of CO and HC emission the vehicles still met the emission standards.
- NO_x emissions showed a downward trend when the vehicles were fed with the emulsions: in any case the resulted to be quite small (NO_x emissions are usually not very sensitive to fuel quality).
- As far as particulate emissions are concerned, with the emulsions a large decrease of the emission levels was noticed both over the urban part of the cycle and over the extra-urban part. In terms of total mass the reduction of emissions ranged from a minimum of –31% to a maximum of –45% over the whole NEDC cycle.
- The effects of the emulsions on the emissions resulted to be influenced by the quality of the base diesel fuel to a very small extent. In fact, despite the extreme differences in the properties, the emulsions prepared with the two diesel fuels selected showed a very similar behaviour in terms of variation of emissions.
- Finally, the profile of the exhaust gas temperature showed no differences between the diesel fuels and the emulsions. As a consequence, the efficiency of the catalyst that depends on the temperature was not adversely affected by the emulsions.

References

1. "High pressure liquid chromatographic method for routine analysis of major parent polycyclic aromatic hydrocarbons in suspended particulate matter". Dong, M., Locke, D. C.; *Anal. Chem.*, 1976. Vol. 48, no. 2, 368-371.
2. "Measurement of Polycyclic Aromatic Hydrocarbons Associated with Size-Segregated Atmospheric Aerosols in Massachusetts". Allen, J. O, Dookeran, N. M.; *Environ. Sci. Technol.*, 1996, Vol. 30, no. 3, 1023-1031.
3. "Composition of Light-Duty Motor Vehicle Exhaust Particulate Matter in Denver Colorado Area". S. H. Cadle, P. A. Mulawa, E. C. Hussanger, K. Nelson, R. Ragazzi, R. Barret, G. L. Gallagher, D. R. Lawson, K. T. Knapp, R. Snow, *Environ. Sci Technol*, 1999, 33, 2328-2339.
4. "Multivariate analysis of Exhaust Emissions from Heavy-Duty Diesel Fuels". M. Sjogren, H. Li, U. Rannug, R. Weterholm; *Environ.Sci Technol*, 1996, 30, 38-49.].
5. "Report of the Committees on Toxicity, Mutagenicity, Carcinogenicity of Chemicals in Food, Consumer Products and the Environment". Department of Health, UK Government, 1996
6. "Provisional guidance for Quantitative Risk Assessment of Polycyclic Aromatic Hydrocarbons", U.S. EPA, 1989; U.S. EPA, 1991; Van der Berg et al., 1998
7. 1. X. Xu, L.L.P. van Stee, J. Williams, J. Beens, M. Adahchour, R.J.J. Vreuls, U.A.Th. Brinkman and J. Lelieveld: "Comprehensive two dimensional gas chromatography (GCxGC) measurements of volatile organic compounds in the atmosphere", *Atmos. Chem. 3* (2003) 665 (www.atmos-chem-phys.org/acp/3/665/ ; www.copernicus.org)
8. 2. A. Borbon, H. Fontaine, N. Locoge, M. Veillerot and J.C. Galloo: "Developing receptor modeling for non methane hydrocarbon characterization in urban air. – Part I: source identification", *Atmos. Environ.* 37 (2003) 4051
9. 3. A. Borbon, H. Fontaine, N. Locoge, M. Veillerot and J.C. Galloo: "Developing receptor modeling for non methane hydrocarbon characterization in urban air. – Part II: source apportionment", *Atmos. Environ.* 37 (2003) 4065
10. 4. "Guidance document for the implementation of the new Ozone Directive" (available at <http://europa.eu.int/comm/environment/air/cafe>).
11. 5. W.P.L. Carter "Development of ozone reactivity scales for volatile organic compounds". *J. Air Waste Manage. Assoc.*, 44 (1994) 881-899.
12. Latella, A., Stani G., Cobelli, L., Duane M., Junninen, H., Astorga, C. Larsen, B. R., Semicontinuous GC analysis and Receptor Modeling For Source Apportionment of ozone precursor hydrocarbons in Bresso, Milan 2003. *J. Chromatography A*, 1071 (2005)29-39.
13. EPEFE (1995) European programme on emissions, fuels and engine technologies. EPEFE Report on behalf of ACEA and EUROPIA
14. SAE paper No. 982486, "Diesel fuel effects on emissions: towards a better understanding"
15. K. Owen, T. Coley, "Automotive Fuels Handbook", Published by Society of Automotive Engineers, Inc.
16. CONCAWE, " Fuel Quality, Vehicle Technology and their Interactions", Concawe Report no.99/55, Concawe, Brussels
17. CONCAWE, "Motor vehicle emission regulations and fuel specifications, Part 1, 2002/203 update", Concawe Report no.9/04, Concawe, Brussels

-
18. J. B. Heywood, "Internal Combustion Engine Fundamentals" McGraw- Hill Publishing Company
 19. SAE paper No. 972894, "Influence of Fuel Properties on Exhaust Emissions from Advanced Heavy-Duty Engines Considering the Effect of Natural and Additive Enhanced Cetane Number"
 20. CONCAWE, "Measurement of the number and mass weighted size distributions of exhaust particles emitted from european heavy duty engines", Concawe Report no.01/51, Concawe, Brussels
 21. CONCAWE, "Evaluation of diesel fuel cetane and aromatics effects on emissions from euro-3 engines", Concawe Report no. 04/02, Concawe, Brussels
 22. CONCAWE, "A study of the number, size & mass of exhaust particles emitted from european diesel and gasoline vehicles under steady-state and European driving cycle conditions", Concawe report no. 98/51, Concawe, Brussels
 23. SAE paper No. 2004-01-1880, "Fuel effects on regulated emissions from advanced diesel engines and vehicles"
 24. "The health effects of fine particles: key questions and 2003 review", Health Effect Institute, HEI Communication no. 8
 25. ACEA, "ACEA programme on emissions of fine particles from passenger cars", ACEA Report December 1999
 26. ACEA et others, "World-Wide Fuel Charter", December 2002
 27. DETR/SMMT/CONCAWE Particulate Research Programme, May 2001
 28. WHO. Health Aspects of Air Pollution with Particulate Matter, Ozone and Nitrogen Dioxide, Bonn, Germany, 2003.
 29. Medina, S.; Plasencia, A.; Ballester, F.; Muecke, H.G.; Schwartz. J. J. *Epidemiol. Community Health*. 2004, 58, 831.
 30. Kaiser, R.; Romieu, I.; Medina, S.; Schwartz, J.; Krzyzanowski, M.; Nino Künzli, N. *Environ. Health: A Global Access Science Source*. 2004, 3, 1.
 31. EPA. Health Assessment Document for Diesel Engine Exhaust EPA/600/8-90/057F. National Center for Environmental Assessment, Washington, DC. 2002.
 32. Crookes R.J.; Kiannejad F.; Nazha M.A.A. *Energy Conversion and Management*, 1997, 38, 1785.
 33. Marwan, A.A; Rajakaruna. N.H; Wagstaff, S.A. The Use of Emulsion, Water Induction and EGR for Controlling Diesel Engine Emissions. SAE Technical Papers 2001-01-1941. SAE, Warrendale, PA, 2001.
 34. Janakiraman. G.; Johnson, J.H; James, S.T; Cuong. P. W.; Khan, T.H.A; Leddy, D.G. Oxidation Catalytic Converter and Emulsified Fuel Effects on Heavy-Duty Diesel Engine Emissions. SAE Technical Papers 2002-01-1277. SAE, Warrendale, PA, 2002.
 35. Hall, D.; Thorne, C.; Goodier, S. An Investigation Into the Effect of a Diesel/Water Emulsion on the Size and Number Distribution of the Particulate Emissions From a Heavy-Duty Diesel Engine. SAE Technical Paper 2003-01-3168, SAE, Warrendale, PA, 2003.
 36. Bertola, A.; Boulouchos, K. Influence of Water-Diesel Fuel Emulsions and EGR on Combustion and Exhaust Emissions of Heavy-Duty, Di-Diesel Engines Equipped With Common-Rail Injection System. SAE Technical Paper 2003-01-3146. SAE, Warrendale, PA, 2003
 37. EPA. Impacts of Lubrizol's PuriNOx Water/Diesel Emulsion on Exhaust Emissions from Heavy-Duty Engines Draft Technical Report. Assessment and Standards Division Office of Transportation and Air Quality. U.S. Environmental Protection Agency, EPA420-P-02-007 December 2002.
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38. IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans. Volume 34. Polynuclear Aromatic Compounds. International Agency for Research on Cancer, Lyon, France, 1984.
 39. Astorga, C.; Suurballe, A.; Bech Olsen, M.; Vialaton, D.; Dilara, P.; De Santi, G.; Larsen, B.R. Development of a protocol for the analysis of toxic PAHs, azarenes, and their nitro-, hydroxyl-, and oxo-derivatives in emission exhaust and ambient PM. EUR 20560 EN. European Communities, Brussels, 2003.
 40. Larsen, B.R.; Astorga, C.; Baglio, D.; Brussol, C.; Duane, M.; Kotzias, D. Characterisation of engine exhaust particulate fingerprints and the contribution to air quality. EUR 19047 EN. European Communities, Brussels, 2000.
 41. EPA. Provisional guidance for Quantitative Risk Assessment of Polycyclic Aromatic Hydrocarbons, U.S. Environmental Protection Agency, Washington, 1989.
 42. Latella, A.; Stani G. , Cobelli, L. , Duane M. , Junninen, H., Astorga, C. Larsen, B. R. Journal of Chromatography. (2004, in print)
 43. B. R. Larsen (ed). Proceedings of the International Expert Meeting on Measurement of Ozone Precursor Volatile Organic Compounds (VOCs), Ispra (VA), Italy. March 6-7. 2003, EUR 21056 EN. European Communities, Brussels, 2004.
 44. Norbeck, J.M. Evaluation of factors that affect diesel exhaust toxicity. Final Report contract No. 94-312, California Air Resources Board, 1998.
 45. CARB. Multi-Media Assessment of Lubrizol's PuriNOx Water/Diesel Emulsion. California Environmental Protection Agency. California, 2004.
 46. Johansen, K.; Gabrielsson, P.; Stavnsbjerg, P.; Bak, F; Andersen, E.; Autrup, H. Effect of upgraded diesel fuels and oxidation catalysts on emission properties, especially PAH and genotoxicity. SAE Technical Paper No. No. 973001, SAE, Warrendale, PA, 1997.
 47. Turrio-Baldassarri, L; Battistellia, C.L; Contia, L.; Crebellia, R.; De Berardisa, B.; Iamicelia, A.; Gambino, M.; Iannaccone, S. Sci. Tot. Environ. 2004, 327, 147.
 48. Tancell, P.J.; Rhead, M.N.; Trier, C.J.; Bell, M.A.; Fussey, D.E.. The sources of benzo(a)pyrene in diesel exhaust emissions. Sci. Tot. Environ. 1995, 162, 179.
 49. CONCAWE, "Polycyclic Aromatic hydrocarbons in automotive exhaust emissions and fuels", Concawe Report 98/55, Bruxelles, Belgium, 1998.
 50. Westerholm, R.N.; Christensen, A.; Tornqvist, M.; Ehrenberg, L.; Rannug, U.; Sjogren, M.; Rafter, J.; Soontjens, C.; Almen, J.; Gragg, K. Comparison of exhaust emissions from Swedish environmental classified diesel fuels (MK1) and european program on emissions fuels and engine technologies (EPEFE) reference fuels: a chemical and biological characterization with viewpoint on cancer risk. Environ. Sci. Technol 2001, 35, 1748.
 51. UK National Atmospheric Emission Inventory. UK Department of the Environment, Transport and the Regions. 2004.
 52. D E Hall, D J King, T D B Morgan, S J Baverstock, P Heinze, B J Simpson. (1998) "A Review of Recent Literature Investigating the Measurement of Automotive Particulate; the Relationship with Environmental Aerosol, Air Quality and Health Effects", SAE Paper No. 982602. Warrendale PA: Society of Automotive Engineers
 53. K. Willeke, P.A. Baron, "Aerosol Measurement: Principles, Techniques and Applications", Van Nostrand Reinhold, New York
 54. Hinds, "Aerosol Technology, Properties, Behavior, and Measurement of Airborne Particles", A Willey – Interscience Publication, John Wiley & Sons, Inc.
 55. EPA - EPA/600/P-97/001F April 1998 Carcinogenic Effects of Benzene: An Update
 56. Toxicological review of benzene (non cancer effects) , (CAS No. 71-43-2)
 57. EPA - Health Assessment of 1,3-Butadiene EPA/600/P-98/001F October 2002
-

-
58. Nazha MAA, Crookes RJ. Effect of water content on pollutant formation in a burning spray of water-in-diesel fuel emulsion. Proceedings of the 20th Symposium (International) on combustion. The Combustion Institute; 1984. p. 2001-10
 59. Cook DH, Law CK. Preliminary study on the utilization of water-in-oil emulsions in diesel engines. Combust Sci Technol 1978;18 (6):217-21
 60. Westerholm, R. and Li, H., 1994. A multivariate statistical analysis of fuel-related polycyclic aromatic hydrocarbon emissions from heavy-duty diesel vehicles. Environ Sci Technol 28, pp. 965–972
 61. Barnaud F, Schmelzle P, Schulz P. Aquazole™ :An original Emulsified Water-Diesel Fuel for Heavy-Duty Applications. SAE 2000-01-1861.
 62. R.J.A. Kersten et al. A study into the explosive boiling potential of thermally stratified liquid-liquid systems that result from runaway reactions. 10th International Symposium on loss prevention and safety promotion in the process industries, 19-21 June 2001, Stockholm, Sweden.
 63. J.C.Lasheras Torralba. Disruptive vaporization and burning of emulsified and multicomponent fuel droplets. Princeton University, USA. OSTI ID: 5532362.
 64. S. Glod et al. An investigation of microscale explosive vaporization of water on an ultrathin Pt wire. International journal of Heat and Mass Transfer 45 (2002) 367-379.
 65. A. Elgowainy, N. Ashgriz. Microexplosion of emulsified fuel drops. <http://www.mie.utoronto.ca/labs/MUSSL/incineration.htm#explosion>.
 66. E. D. Rogdakis, N. A. Bormpilas, I. K. Koniakos – Predicted Thermodynamic and Physical Boundary of the Superheated and Stretched Water by some EOS and the Fluctuation Theory of Relaxation
 67. C. E. Brennen. Cavitation and bubble dynamics. Oxford University press 1995.
 68. Mattiello M, Cosmai L, Pistone L. Experimental evidence for microexplosions in water/fuel oil emulsion flames inferred by laser light scattering. Proceedings of the 24th Symposium (International) on combustion. The Combustion Institute; 1992. p. 1573-8.
 69. T.Kadota, H.Yamasaki. Recent advances in the combustion of water fuel emulsion. Progress in energy
 70. Daisuke Segawa et al. Water-coalescence in an oil-in-water emulsion droplet burning under microgravity. Proceedings of the Combustion Institute, vol. 28 2000, pp. 985-990.
 71. Hong-zhi Sheng, Li Chen, Cheng-kang Wu. The droplet Group Micro-Explosions in W/O Diesel Fuel Emulsion Sprays. SAE technical paper series 950855
 72. Franz B, Roth P. Injection of a H₂O₂ /water solution into the combustion chamber of a direct injection diesel engine and its effect on soot removal. Proceedings of the Combustion Institute, vol. 28 2000.pp. 1219-1225.
 73. Abu-Zaid, M. Performance of a single cylinder, direct injection Diesel engine using water fuel emulsions. Energy Conversion and Management, 2004. vol 45, 5, p. 697-705
 74. Schmelzle P, Chandes K. The Challenge Facing AQUAZOLE: Compatibility With New Engine and DPF Technologies. SAE paper 2004-01-1885
 75. Law CK. On the fire resistant nature of oil/water emulsions. Fuel 1981;60:998-9.
 76. C. Arcoumanis. Auto/Oil, 2000a – A technical study on fuels technology related to Auto Oil II Programme. Final report. December 2000.
 77. Aerosol dynamics, laboratory and on-road studies. Prepared by David B. Kittelson, Ph.D., Winthrop F. Watts, Jr., Ph.D. and Megan Arnold University of Minnesota July 31, 1998
 78. 132nitro-, hydroxyl-, and oxo-derivatives in emission exhaust and ambient PM. EUR 20560 EN. European Communities, Brussels, 2003.
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-
79. Gollahalli SR ,Rasmussen ML, Moussavi SJ. Combustion of drops and sprays of No.2 diesel oil and its emulsions with water. Proceedings of the 18th Symposium (International) on combustion. The Combustion Institute; 1981. p.349-60.

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EUR21380 EN – DG Joint Research Centre, Institute for Environment and Sustainability

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Larsen, Bo

Luxembourg: Office for Official Publications of the European Communities

2005 – 71 pp. – 21 x 29.7 cm

EUR - Scientific and Technical Research series;

ISBN 92-894-9744-0

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