Biodiesel as a control strategy for reducing exposure of underground miners to diesel aerosols

Part I: Effects on physical and chemical properties of emitted aerosols

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Introduction

- Fuels derived from biomass, commonly known as a biodiesel, are considered as a viable alternative to petroleum derived diesel fuels.

- Biodiesel fuels most widely used in the U.S. are made of long-chain, fatty acid methyl esters (FAME) obtained from vegetable oils and animal fats.

- FAME biodiesel is currently used by a relatively large number of underground mining operations in the U.S. to control exposures of miners to aerosols and gases emitted by diesel-powered vehicles.

Objective

- Previous field and laboratory studies showed that FAME biodiesel fuels have potential to reduce concentrations of diesel particulate matter (DPM), particularly elemental carbon (EC) in underground mines.
  - Bugarski, A.D., Cauda, E.G., Janisko, S.J., Patts, L.D., Hummer J.A., Terrillion, T., Westover C [2011]. 17th Annual Mining Diesel Emissions Council (MDEC) Conference, Toronto, Ontario, Canada, October 4-7.
  - Bugarski, A.D., Cauda E., Janisko, S.J., Hummer, J.A., Patts, L.D. [2010]. Journal of Air and Waste Management Association, 60, 237-244.
- The National Institute for Occupational Safety and Health (NIOSH) conducted a laboratory study in order to quantify and characterize the effects of soy derived FAME biodiesel fuels on physical, chemical and toxicological properties of aerosols emitted by diesel engines equipped with diesel oxidation catalytic converter (DOC),
- The effects of two biodiesel blends (B20, B50) and neat biodiesel (B100) were compared with the corresponding effects of petroleum based ultralow sulfur diesel (ULSD) fuel.

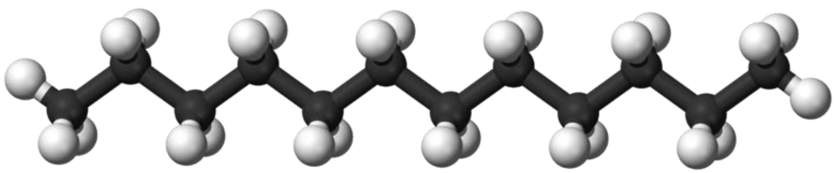
Fuels Used in the Study

- Soy-based FAME biodiesel supplied by Peter Cremer NA, Cincinnati, OH.
- ULSD supplied by Gutman Oil.
- The results of fuel analysis performed on the fuels by Bentley Tribology Services, Minden, NV are given in the following table:

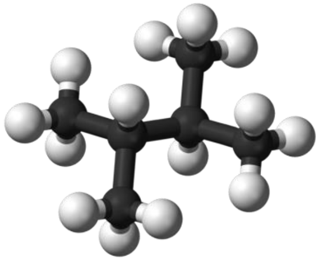
Fuel Property	Test Method	ULSD	B100
Fatty Acid Methyl Ester Content [%]	ASTM 7371	N/A	100
Heat of Combustion [BTU/gal]	ASTM D240	140402	128762
API Gravity @ 15.6 °C [°API]	ASTM D1298	35.5	28.8
Cetane Number	ASTM D613	43.3	50.4
Sulfur by UV [ppm]	ASTM D5453	6.52	3.27
Cold Filter Plug Point [°C]	ASTM D6371	-20	-2
Flash Point, Closed Cup [°C]	ASTM D93	70	180

Petroleum based diesel and FAME biodiesel fuels differ substantially in chemical and physical properties.

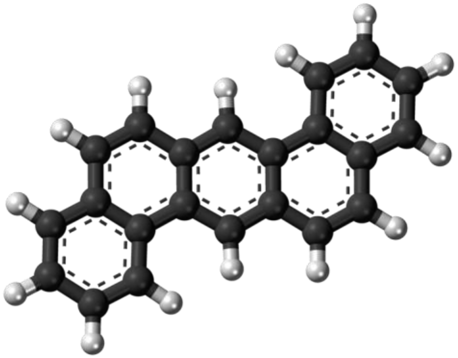
- Petroleum based diesel is made of alkanes (paraffins, C_nH_{2n+2}), alkenes (olefins, C_nH_{2n}), and arenes (aromatic hydrocarbons).
- The general formula would be $C_{12}H_{23}$ ($C_{10}H_{20}$-$C_{15}H_{28}$).



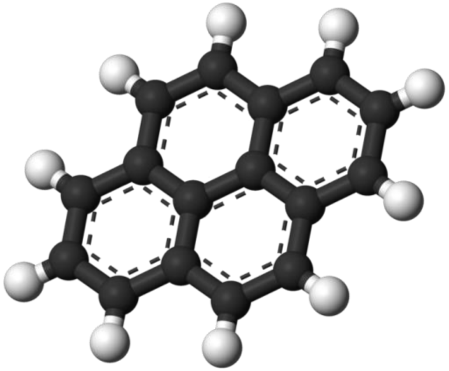
Dodecane



2,3-Dimethylbutane



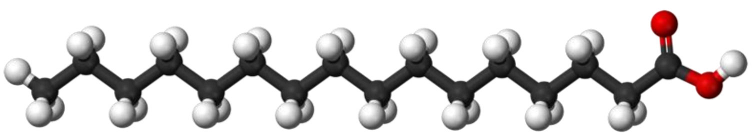
Dibenz(a,h)anthracene



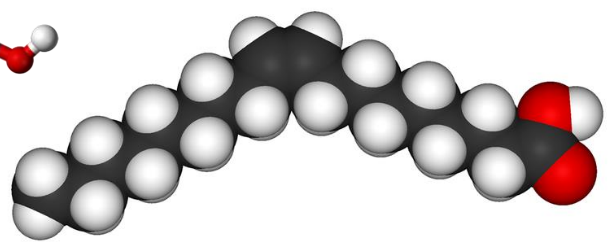
Pyrene

Biodiesel fuels used in the States are made primarily of fatty acids methyl esters.

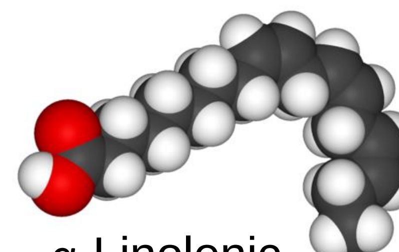
Content of Fatty Acids in FAME Biodiesels	Myristic Acid	Palmitic Acid	Stearic Acid	Oleic Acid	Linoleic Acid	Linolenic Acids
Source	14:0	16:0	18:0	18:1	18:2	18:3
Soybean Oil		6-10	2-5	20-30	50-60	5-11
Corn Oil	1-2	8-12	2-5	19-49	34-62	
Canola Oil		4	1	60	20	13
Palm Oil		44	5	39	10	
Tallow	3-6	24-32	20-25	37-43	2-3	
Yellow Grease	1-2	17	13	55	8	



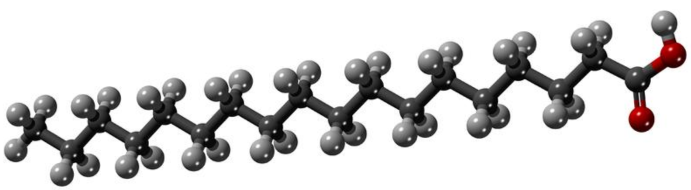
Palmitic



Oleic

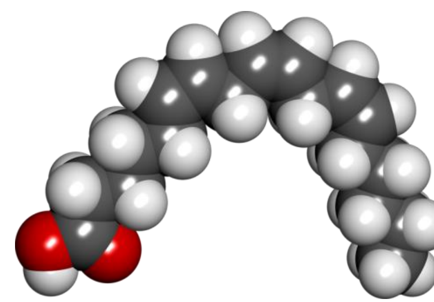


α-Linolenic



Stearic

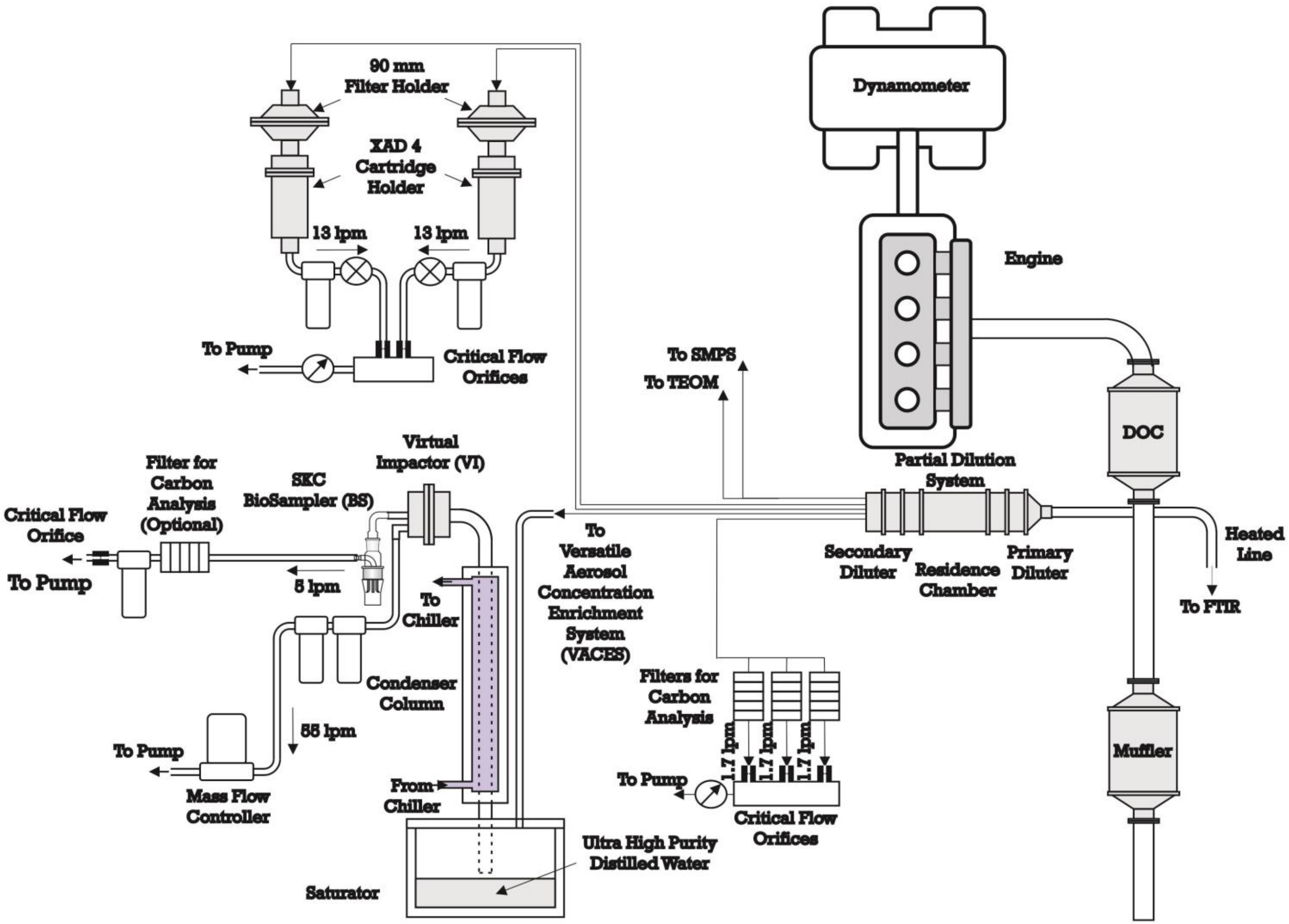
Linoleic



ϒ-Linolenic

Methodology

The experimental work took place at the diesel laboratory at NIOSH OMSHR.



Dynamometer , Engine, and Exhaust Aftertreatment

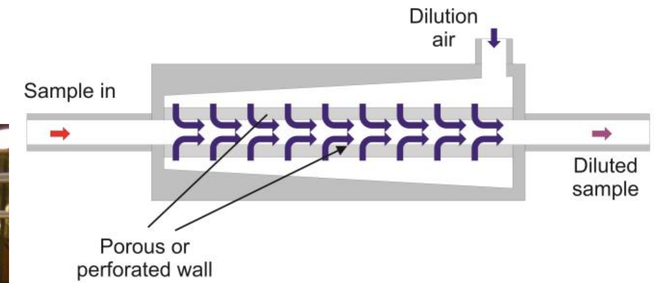
Test Vehicle	Specifications
Dynamometer Manufacturer	SAJ, Pune, India
Dynamometer Model	SE150
Engine Manufacturer	Isuzu
Engine Model	C240
Number of Cylinders	4 (inline)
Engine Displacement	2.4 l
Engine Type	liquid cooled, naturally aspirated
Engine Output	41.8 KW (56 hp)
Exhaust Aftertreatment Supplier	Lubrizol, New Market, ON
Exhaust Aftertreatment Type	diesel oxidation catalytic converter (DOC)

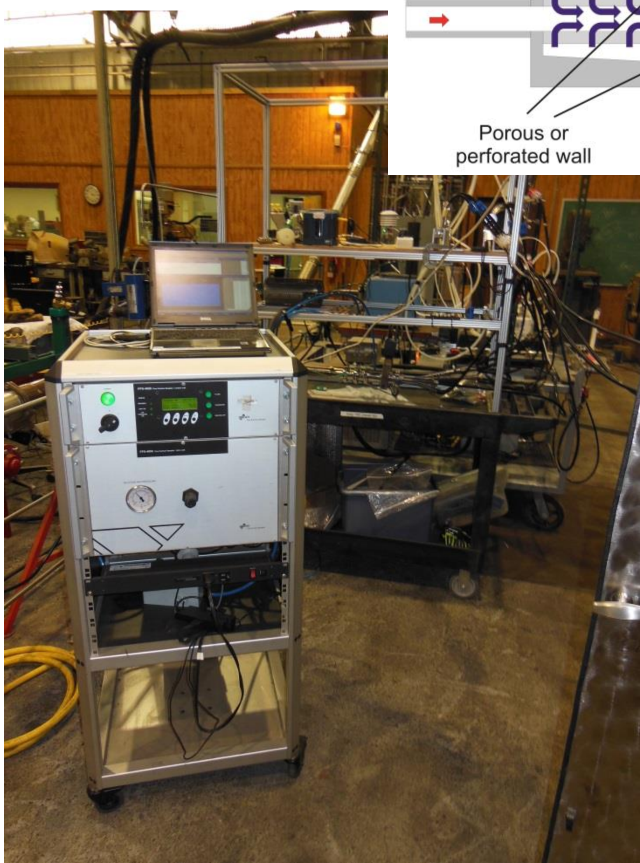
The effects of fuels were evaluated for four steady-state operating conditions.

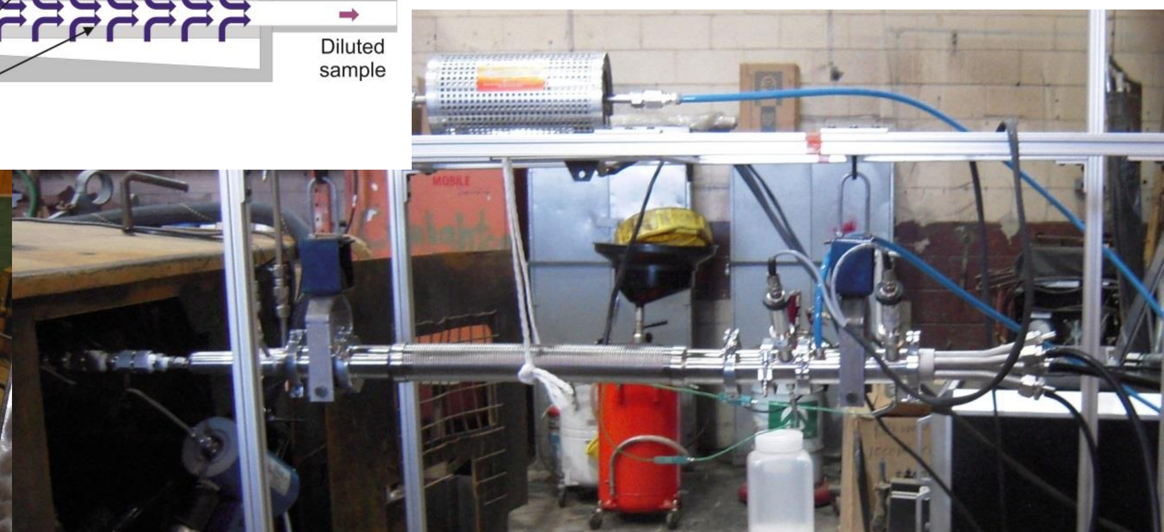
Conditions	Description	Engine Speed	Torque	Power
		rpm	Nm	kW
R50	Rated speed and 50% load	2950	55.6	17.2
R100	Rated speed and 100% load	2950	111.2	34.3
I50	Intermediate speed and 50% load	2100	69.1	14.9
I100	Intermediate speed and 100% load	2100	136.9	30.6

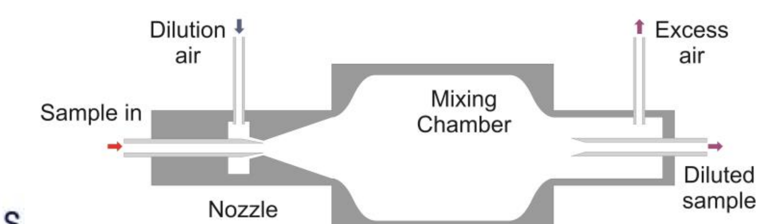
The aerosol sampling and measurements were conducted in the exhaust diluted approximately 30 times using partial dilution system.

- Dekati FPS4000 is designed to dilute exhaust in two stages.
- Primary dilution occurred in perforated disk diluter;
- Secondary dilution was provided by ejector diluter;
- The residence chamber was inserted between those two stages.









Aerosols Sampling and Measurements

- The effects on mass concentrations of elemental carbon (EC) and total carbon (TC) were determined using the results of thermal optical transmittance-evolve gas analysis (TOT-EGA) performed on the filter samples collected from the diluted exhaust.
- Total mass concentrations of aerosols were measured in diluted exhaust using Tapered Element Oscillating Microbalance (Thermo, TEOM 1405).
- Number concentrations and size distributions of aerosols were measured in diluted exhaust using Scanning Mobility Particle Sizer (TSI, Model 3936 SMPS).

Sampling Organic Compounds for Detailed Hydrocarbon Speciation

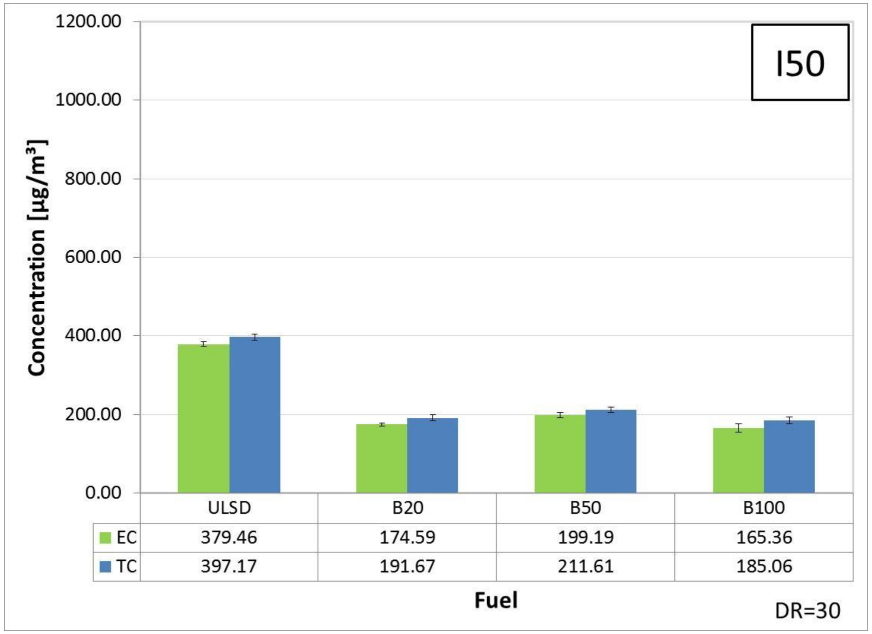
- The effects on selected hydrocarbon species were determined using the results of gas chromatography-mass spectrometry (GC-MS) performed on the filter and resin samples collected from the diluted exhaust.

- The particle-bound samples were collected on 90 mm Teflon -coated glass fiber filters.

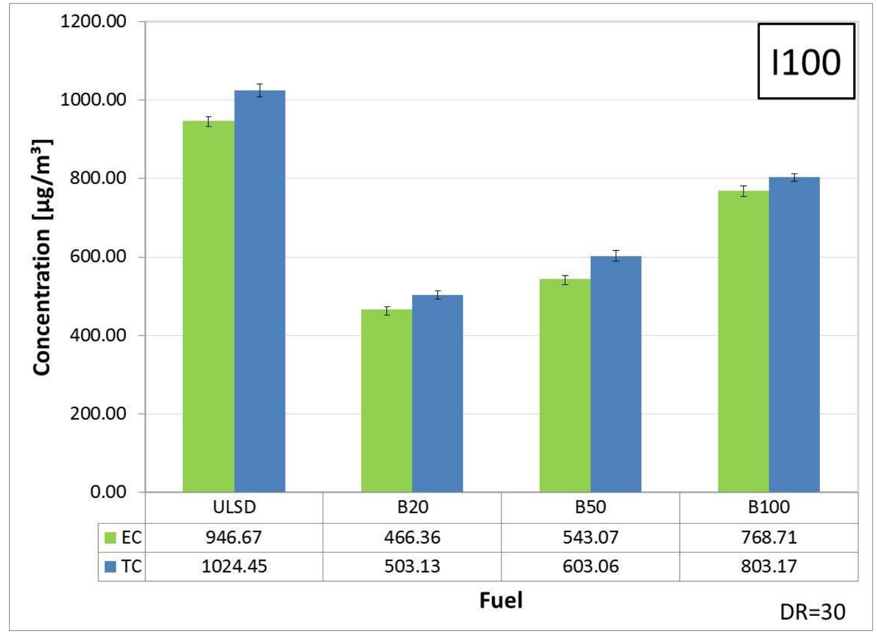
- The semi volatile samples were collected on XAD-4 resin encapsulated in the 50 mm glass cartridge.

Results

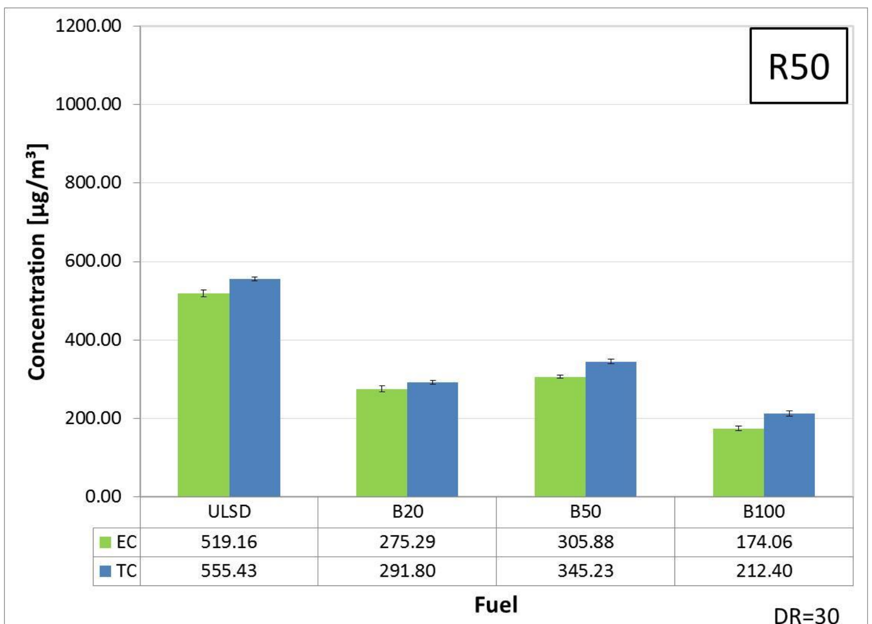
The effects on elemental carbon (EC) and total carbon (TC) concentrations were examined on the results of TOT-EGA analysis performed on the samples collected on quartz fiber filters.



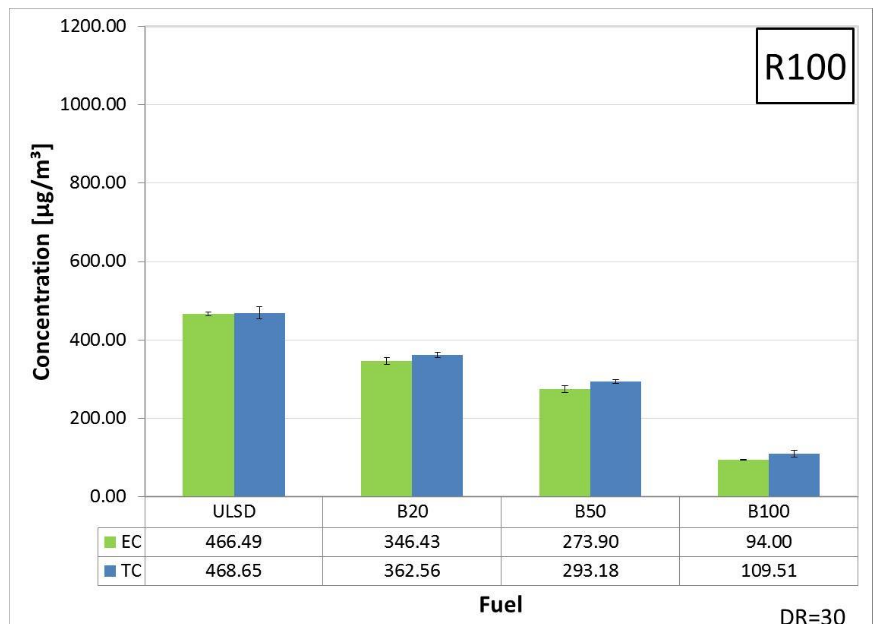
	ULSD	B20	B50	B100
EC	379.46	174.59	199.19	165.36
TC	397.17	191.67	211.61	185.06



	ULSD	B20	B50	B100
EC	946.67	466.36	543.07	768.71
TC	1024.45	503.13	603.06	803.17



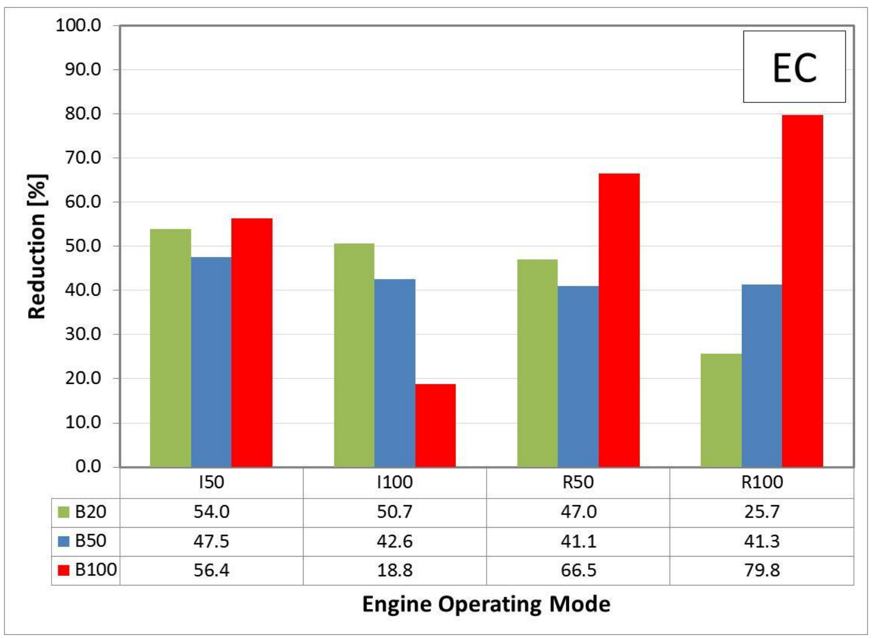
	ULSD	B20	B50	B100
EC	519.16	275.29	305.88	174.06
TC	555.43	291.80	345.23	212.40

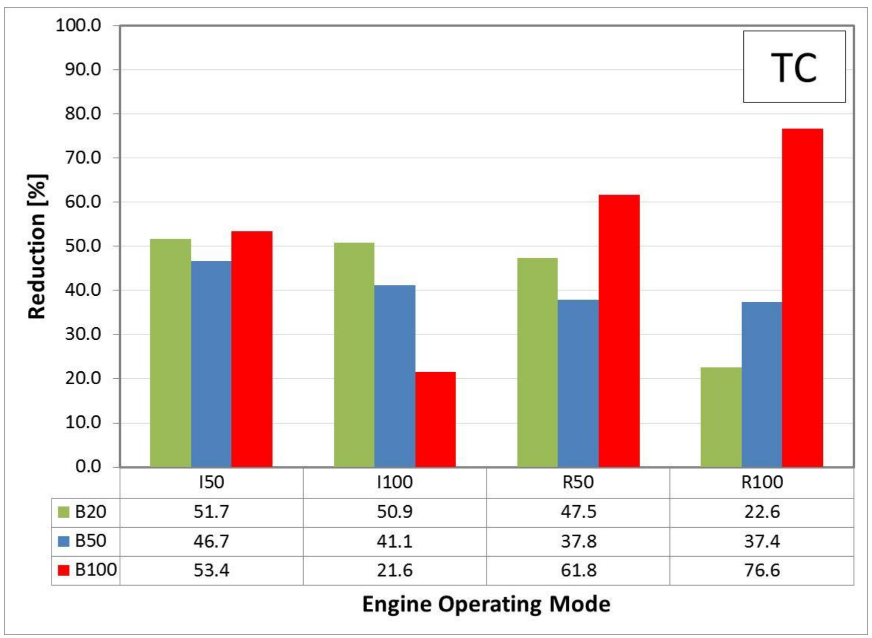


	ULSD	B20	B50	B100
EC	466.49	346.43	273.90	94.00
TC	468.65	362.56	293.18	109.51

In all test cases, the test engine emitted less EC and TC when fueled with B20, B50, and B100 then with ULSD.

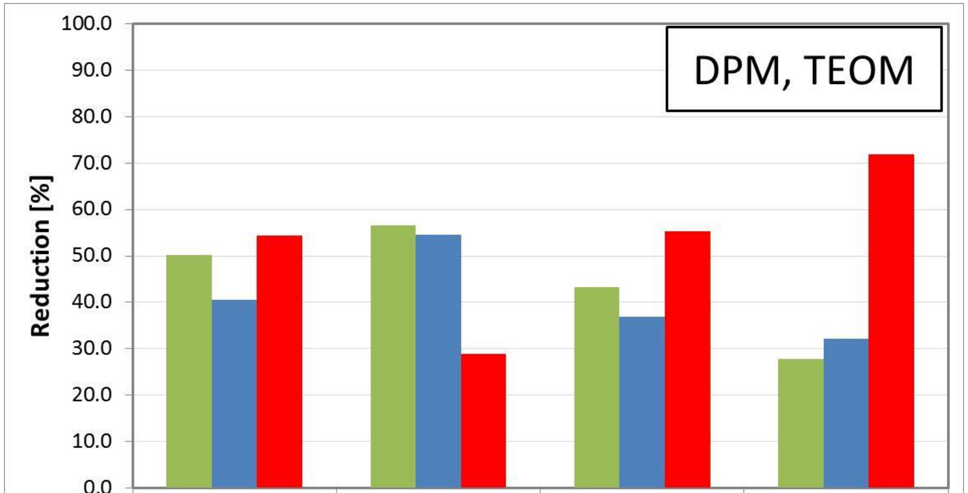
- However, the relative changes in EC and TC concentrations were found to be strongly dependent of the engine operating conditions.
  - For R100 mode, the effects were indirectly proportional to the biodiesel content.
  - On contrary, for I100 mode, the effects were directly proportional to the biodiesel content.
  - For I50 and R50, the EC and TC emissions were lowest for B100, but the trends in relation between biodiesel content and changes were not apparent.





Effects on total mass concentrations of diesel particulate matter (DPM) were assessed using the results of measurements withTEOM 1405.

- The results of TEOM measurements corroborated the results of carbon analysis:
  - In all test cases, the test engine emitted less total DPM when fueled with B20, B50, and B100 then with ULSD.
  - The total DPM concentrations were strongly dependent of the engine operating conditions.
  - The effects on total DPM mass concentrations were in some cases directly and in other cases indirectly proportional to the biodiesel content in the fuel.



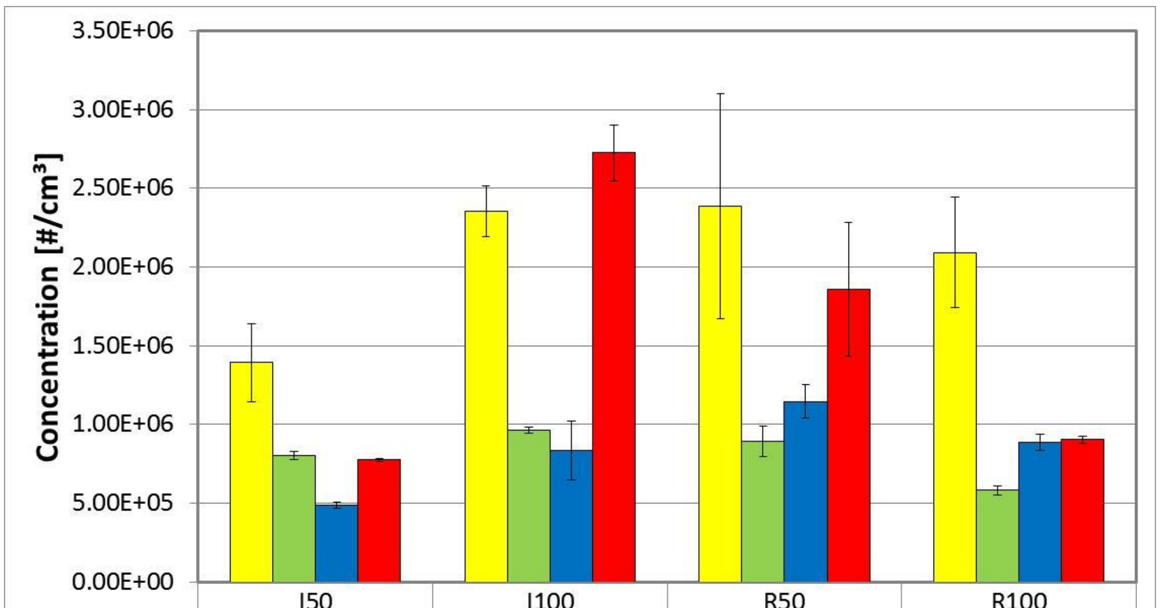
	I50	I100	R50	R100
B20	50.2	56.5	43.2	27.8
B50	40.6	54.6	36.9	32.2
B100	54.3	28.8	55.2	71.9

Engine Operating Mode

The effects on total number concentrations of diesel aerosols were assessed using the results of measurements with SMPS 3936.

- The total number concentrations were strongly dependent of the engine operating conditions.

- With exception of B100 case for I100 conditions, the engine emitted less aerosols by number when fueled with B20, B50, and B100 then with ULSD.

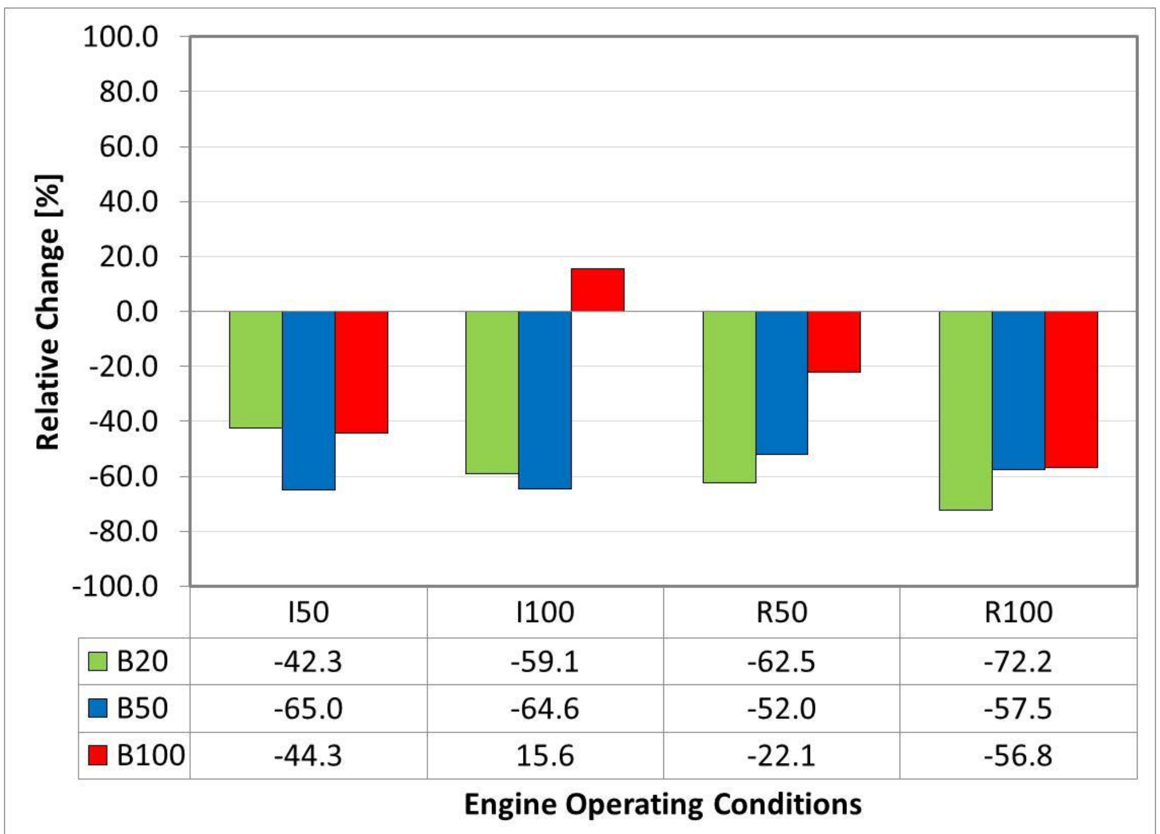


	I50	I100	R50	R100
ULSD	1.39E+06	2.36E+06	2.39E+06	2.09E+06
B20	8.04E+05	9.64E+05	8.95E+05	5.82E+05
B50	4.87E+05	8.34E+05	1.15E+06	8.89E+05
B100	7.75E+05	2.73E+06	1.86E+06	9.05E+05

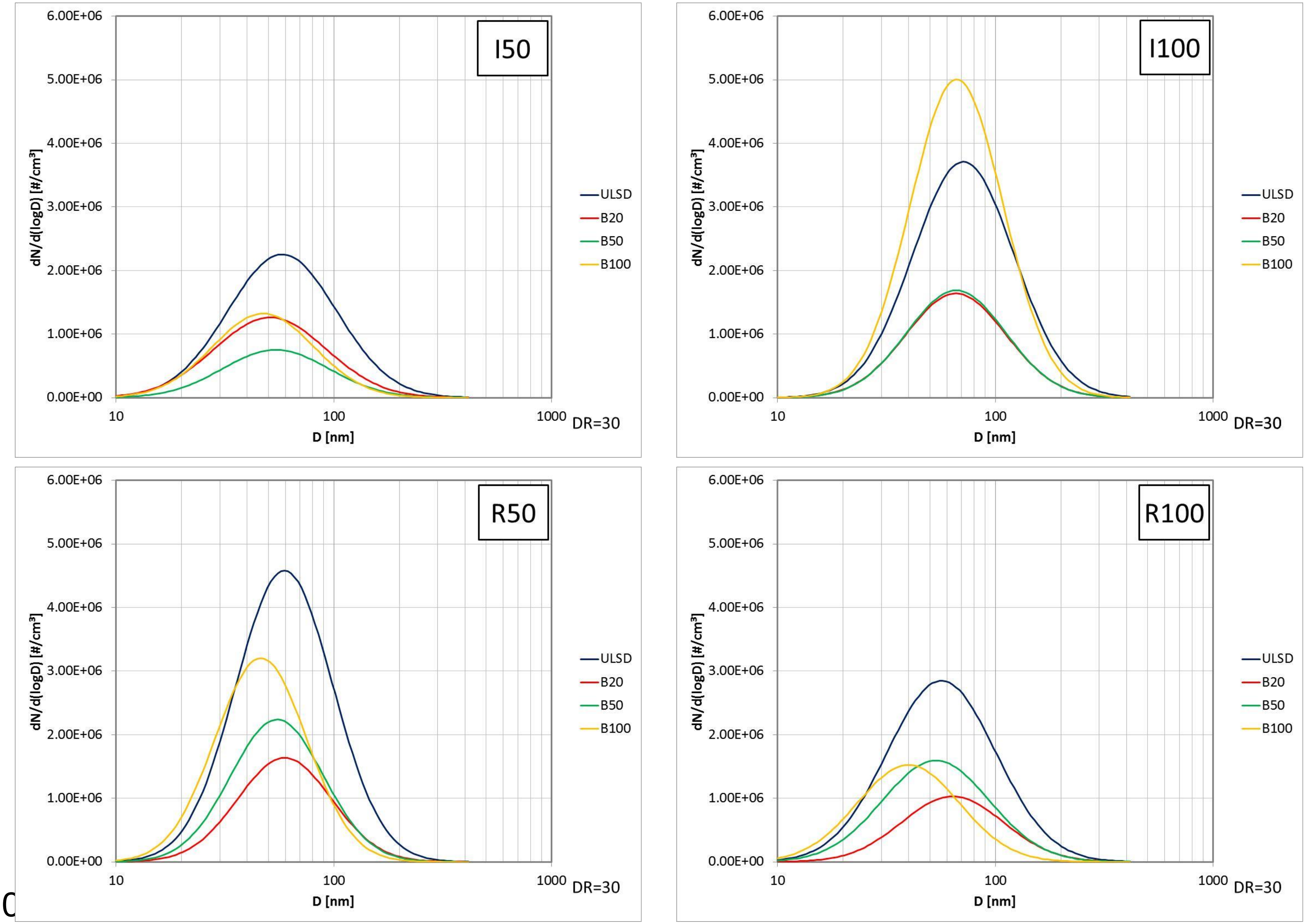
The relative changes in number concentrations were also found to be dependent of the engine operating conditions.

- For I50 and I100, the trends in relation between biodiesel content and changes were not apparent.

- For R50 and R100 mode, the effects on number concentrations were indirectly proportional to the biodiesel content.



The effects on size distribution of aerosols were assessed using the results of selected representative measurements with SMPS 3936



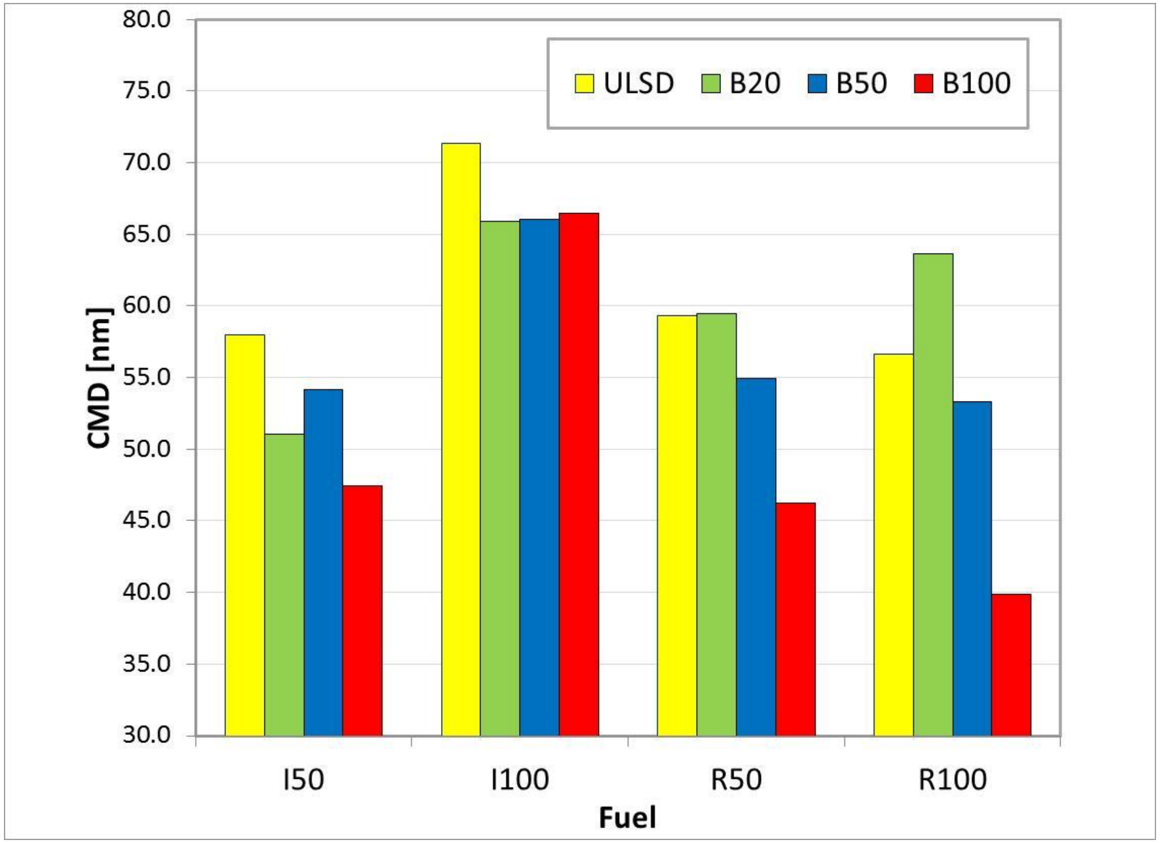
For all test cases, the distributions were single modal.

- In the majority of test cases, the engine emitted the aerosols with largest count median diameters (CMDs) when operated on ULSD and smallest CMDs when operated on B100.

Fuel	Mode	CMD	σ	Total Conc.
		nm	-	#/cm³
ULSD	I50	58.0	1.78	1.41E+06
	I100	71.4	1.71	2.17E+06
	R50	59.3	1.67	2.56E+06
	R100	56.6	1.77	1.78E+06
B20	I50	51.1	1.81	8.13E+05
	I100	65.9	1.70	9.44E+05
	R50	59.5	1.64	8.84E+05
	R100	63.7	1.71	6.02E+05
B50	I50	54.2	1.75	4.60E+05
	I100	66.1	1.69	9.62E+05
	R50	54.9	1.63	1.20E+06
	R100	53.3	1.76	9.79E+05
B100	I50	47.4	1.71	7.72E+05
	I100	66.5	1.63	2.68E+06
	R50	46.3	1.62	1.69E+06
	R100	39.9	1.72	8.97E+05

The effects of fuel on CMDs were relatively minor.

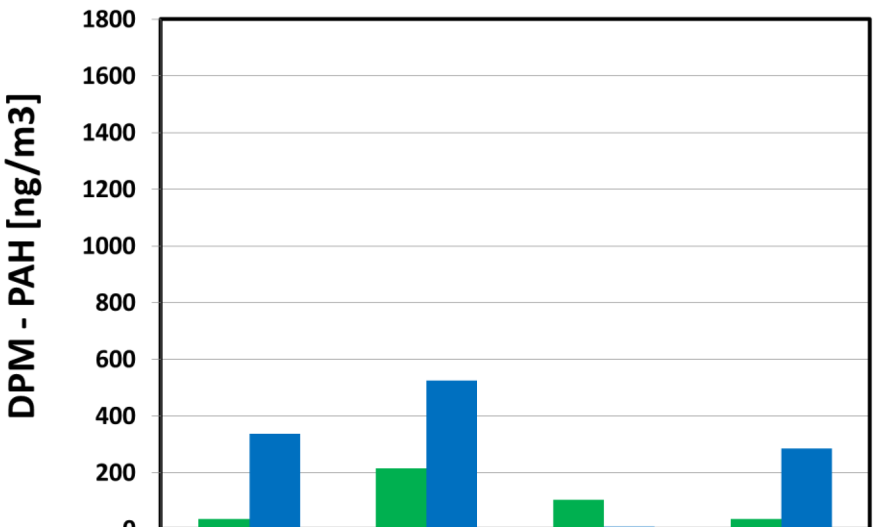
- With few aberrations, CMDs of aerosols in diluted exhaust decreased with increase in biodiesel content in the fuels.



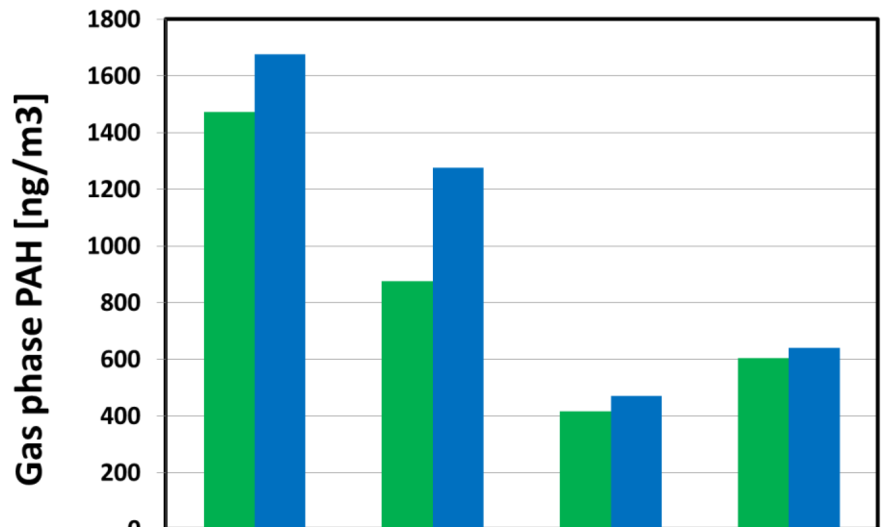
The particulate and semi volatile phase samples collected for I50 and I100 conditions were analyzed for 110 different polycyclic aromatic hydrocarbons (PAHs).

- The PAHs were more abundant in semi-volatile than particle-bound phase.

- In general, the effects of the fuels on PAHs were found to be engine operating conditions dependent.



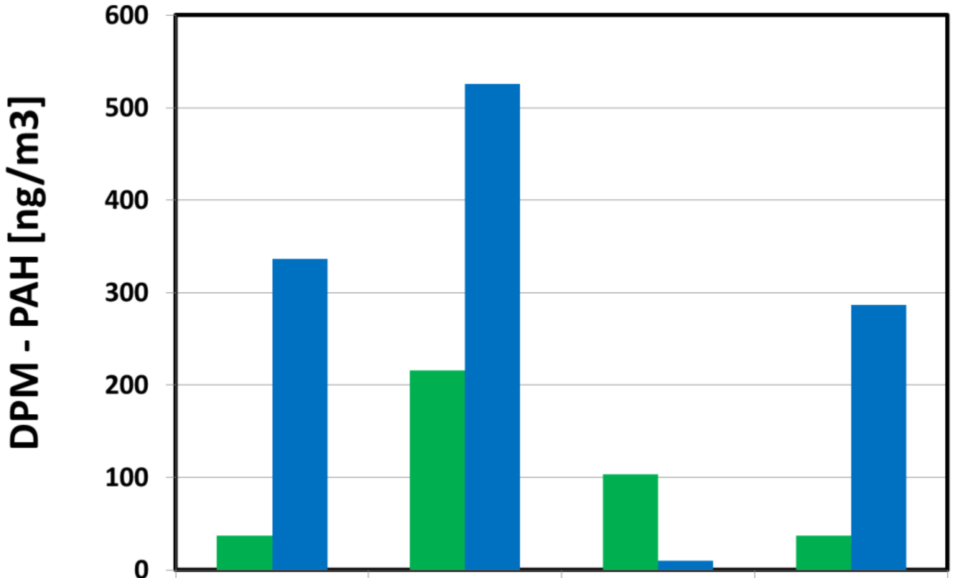
	ULSD	B20	B50	B100
I50	37.5	216.0	103.6	37.2
I100	336.6	525.6	10.0	286.4



	ULSD	B20	B50	B100
I50	1473.7	876.0	416.0	603.5
I100	1675.6	1277.0	471.4	640.9

In general, the concentrations of particle-bound PAHs were higher for the fuels containing biodiesel.

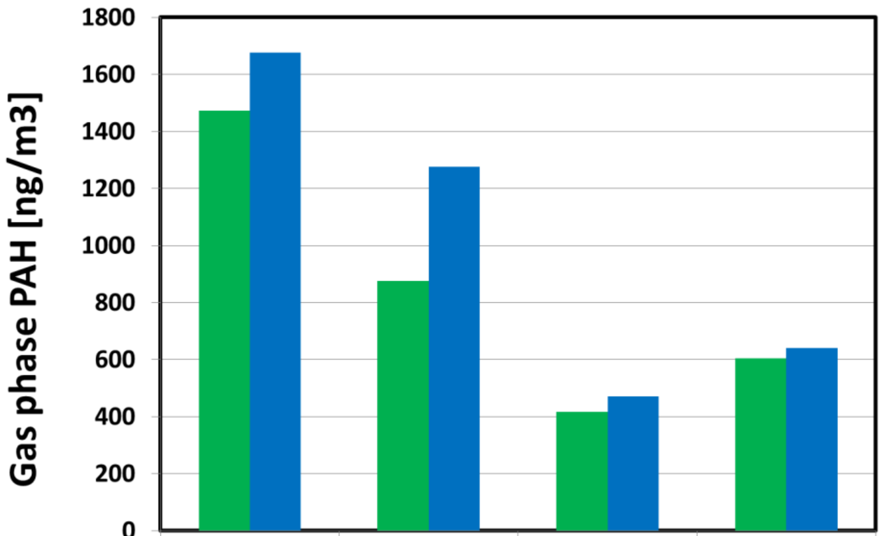
- In the majority of the cases, the concentrations of particle-bound PAHs were higher for I100 than for I50 conditions.
- For both engine operating conditions, the highest concentrations of particle-bound PAHs were observed for B20.



	ULSD	B20	B50	B100
I50	37.5	216.0	103.6	37.2
I100	336.6	525.6	10.0	286.4

In general, the concentrations of semi volatile PAHs were lower for B20, B50, and B100 than for ULSD.

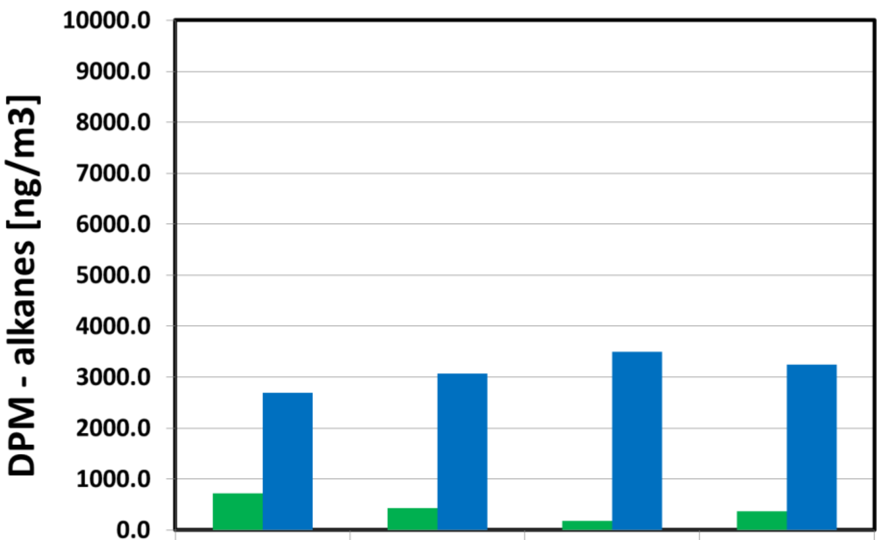
- The concentrations of semi volatile PAHs were in all cases higher for I100 than for I50 conditions.
- However, the trends in fuel effects were similar for I50 and I100 conditions.
- For both conditions, the lowest concentrations of semi volatile PAHs were observed for B50.



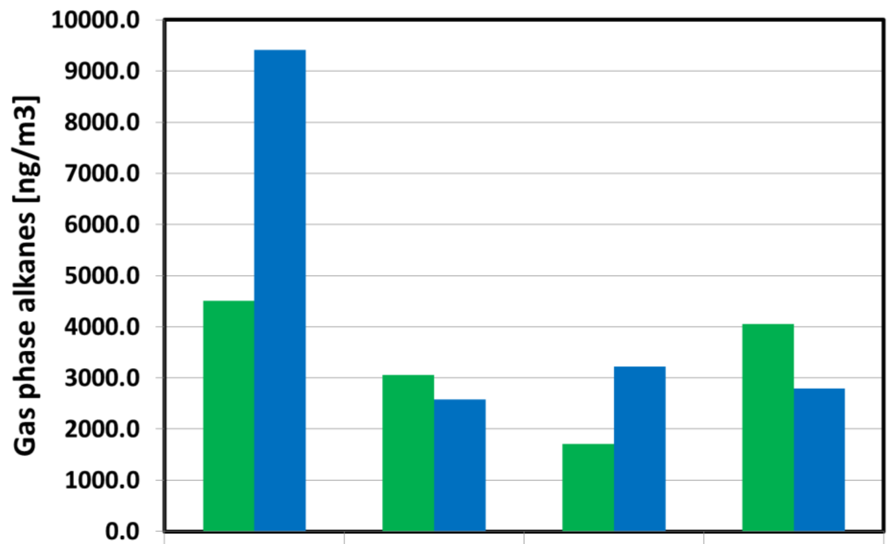
	ULSD	B20	B50	B100
I50	1473.7	876.0	416.0	603.5
I100	1675.6	1277.0	471.4	640.9

The particulate and semi volatile phase samples were also analyzed for 48 different alkanes.

- The effects of the fuels on the alkanes were also found to be engine operating conditions dependent.
- In some cases (all I50 cases and I100/ULSD case), the alkanes were found to be more abundant in semi volatile than particle-bound phase.
- For I100 conditions (B20, B50, and B100), the concentrations of alkanes were similar in particle-bound and semi volatile samples.



	ULSD	B20	B50	B100
I50	714.9	426.5	179.8	370.8
I100	2696.9	3075.0	3497.9	3250.5

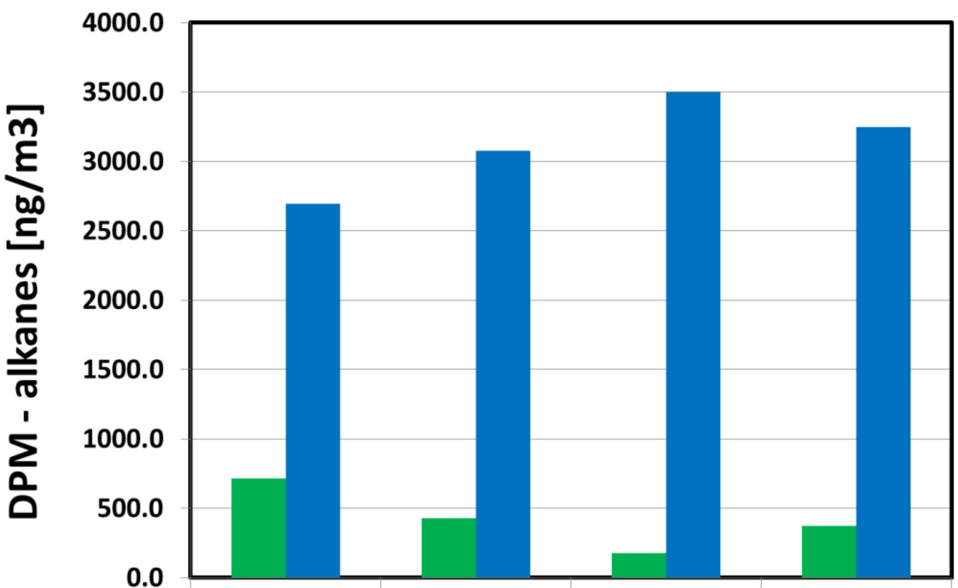


	ULSD	B20	B50	B100
I50	4510.5	3058.7	1705.4	4048.8
I100	9415.9	2577.7	3224.7	2791.0

In all the cases, the concentrations of particle-bound alkanes were higher for I100 than for I50 conditions.

- For I50 conditions, the concentrations of particle-bound alkanes were lower for the fuels containing biodiesel than for ULSD.

- For I100 conditions, the concentrations of particle-bound alkanes were slightly higher for the fuels containing biodiesel, than for neat ULSD.

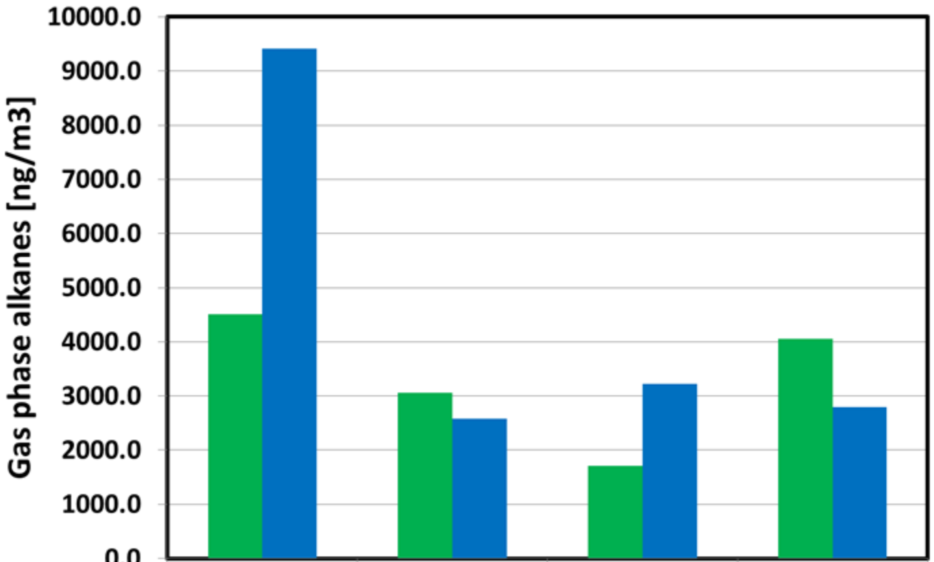


	ULSD	B20	B50	B100
I50	714.9	426.5	179.8	370.8
I100	2696.9	3075.0	3497.9	3250.5

In general, the concentrations of semi-volatile alkanes were lower for B20, B50 , and B100 than for ULSD.

- For I50 conditions, the concentrations of semi volatile alkanes were lowest for B50.

- For I100 conditions, the concentrations of semi volatile alkanes were lowest for B20.

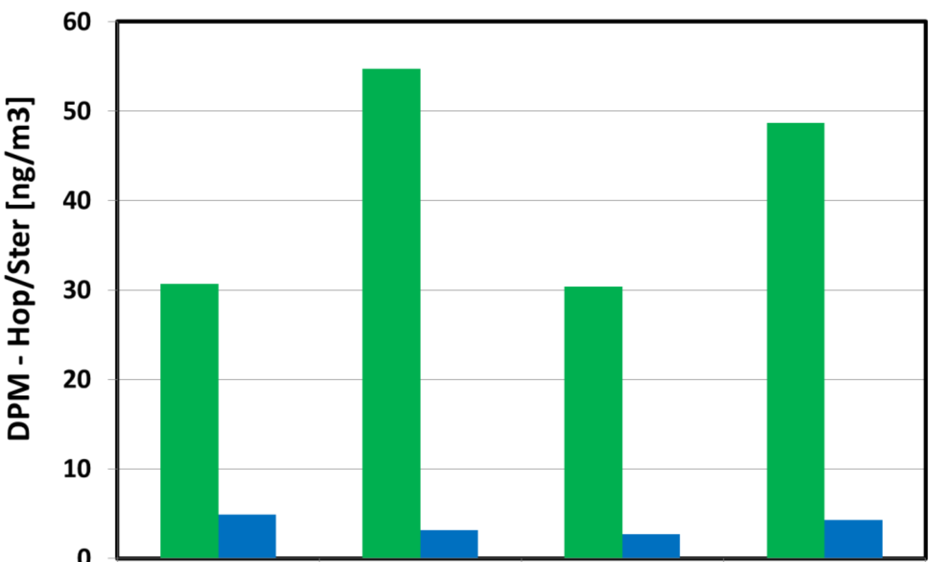


	ULSD	B20	B50	B100
I50	4510.5	3058.7	1705.4	4048.8
I100	9415.9	2577.7	3224.7	2791.0

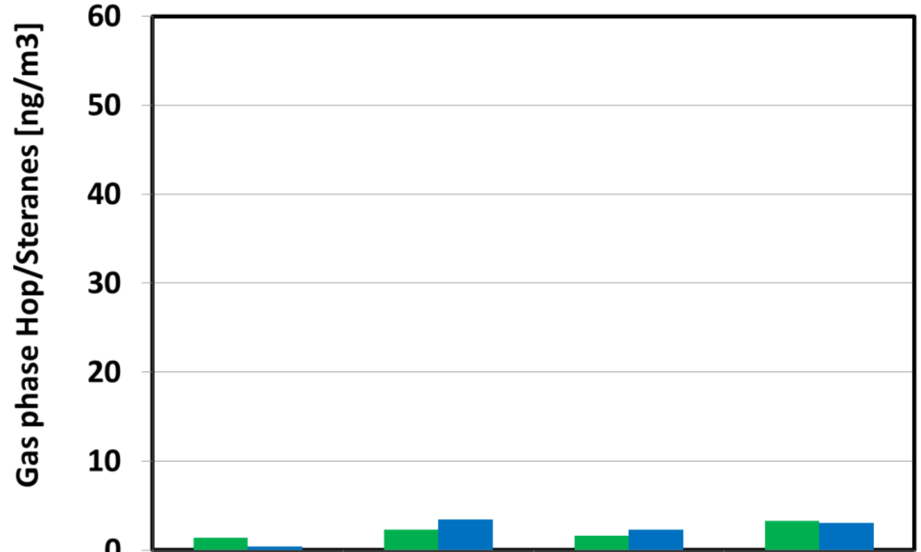
The particulate and semi volatile phase samples were also analyzed for 22 different hopanes and steranes

- The hopanes and steranes, typically traced to lubricating oil, were more abundant in particle-bound than semi volatile phase.

- Engine operating conditions had dramatic effect on concentrations of hopanes and steranes in particulate samples.



	ULSD	B20	B50	B100
I50	30.7	54.7	30.4	48.7
I100	4.9	3.2	2.7	4.3

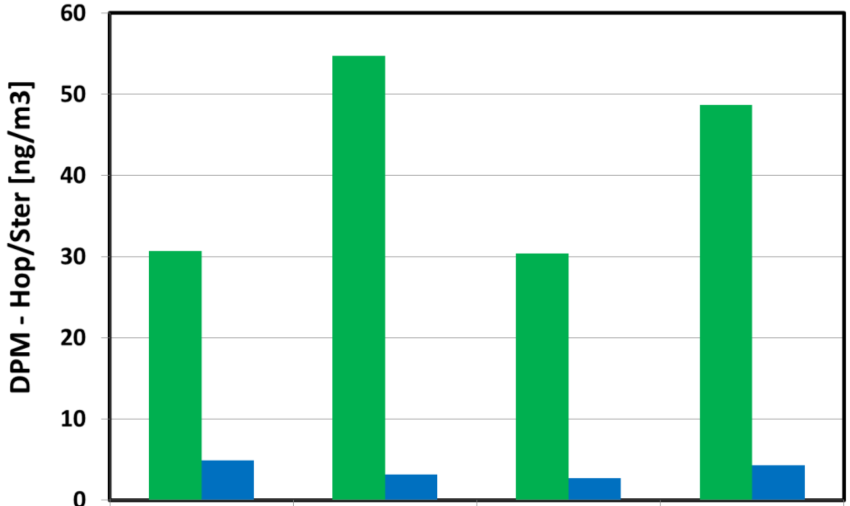


	ULSD	B20	B50	B100
I50	1.4	2.3	1.7	3.3
I100	0.4	3.5	2.3	3.0

In all the cases, the concentrations of particle-bound hopanes and steranes were higher for I50 than for I100 conditions.

- For I50 conditions, the concentrations of particle-bound hopanes and steranes were higher for B20 and B100 and similar for B50 than those observed for ULSD.

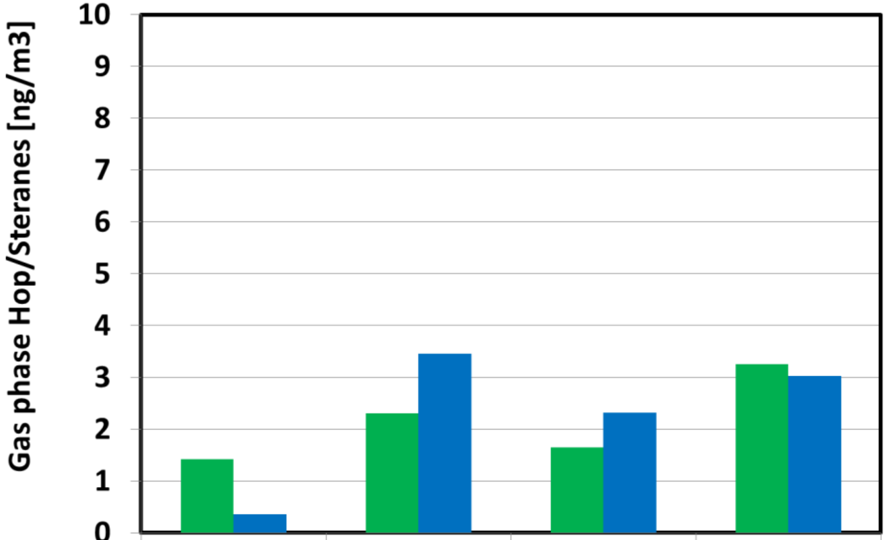
- For I100 conditions, the concentrations of particle-bound hopanes and steranes were slightly lower for the fuels containing biodiesel, than for neat ULSD.



	ULSD	B20	B50	B100
I50	30.7	54.7	30.4	48.7
I100	4.9	3.2	2.7	4.3

The concentrations of hopanes and steranes in semi volatile samples were very low.

- For both I50 and I100 conditions, the concentrations of semi volatile phase hopanes and steranes were higher for the fuels containing biodiesel, than for neat ULSD.



	ULSD	B20	B50	B100
I50	1.4	2.3	1.7	3.3
I100	0.4	3.5	2.3	3.0

PAHs+alkanes+hopahes+steranes

- For I50 conditions, the total concentrations of detected particle-bound organic compounds were lower when engine was using B20, B50, and B100 instead of ULSD. The lowest concentration was observed for B50.

- For I100 conditions, the total concentrations of detected particle-bound organic compounds were on average 15% higher when biodiesel fuels were used in place of ULSD.

- For I50 conditions, use of biodiesel fuels resulted in lower total concentrations of the semi volatile organic compounds. The highest reduction from baseline case (ULSD) of approximately 33 percent was observed for B20.

- At I100 conditions, the total concentrations of semi volatile organic compounds were greatly reduced by the biodiesel blends. The reductions do not appear to be affected by biodiesel content.

Summary

- Therefore, based on the results of this study one can conclude that biodiesel (B20, B50, B100) as a control strategy have potential to:
  - Reduce EC, TC, and DPM mass concentrations;
  - Reduce aerosol number concentrations;
  - Reduce concentrations of semi volatile PAHs and alkanes;
  - Produce aerosols with slightly smaller CMDs.

- However, engine operating conditions and engine type (Durbin et al. 2007) play a major role in defining the characteristics of emissions when using FAME fuels as a control strategy.
  - Durbin DT, Cocker DR III, Sawant AA, Johnson K, Miller JW, Holden BB, Helgeson NL, Jack JA [2007]. Atmos Environ 41: 5647–5658.

- **What about toxicity of aerosols emitted by diesel engines fueled by biodiesel fuels?**

Thank you for your attention!

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The findings and conclusions in this presentation are those of the authors and do not necessarily represent the views of NIOSH. Mention of company names or products does not constitute endorsement by the Centers for Disease Control and Prevention

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