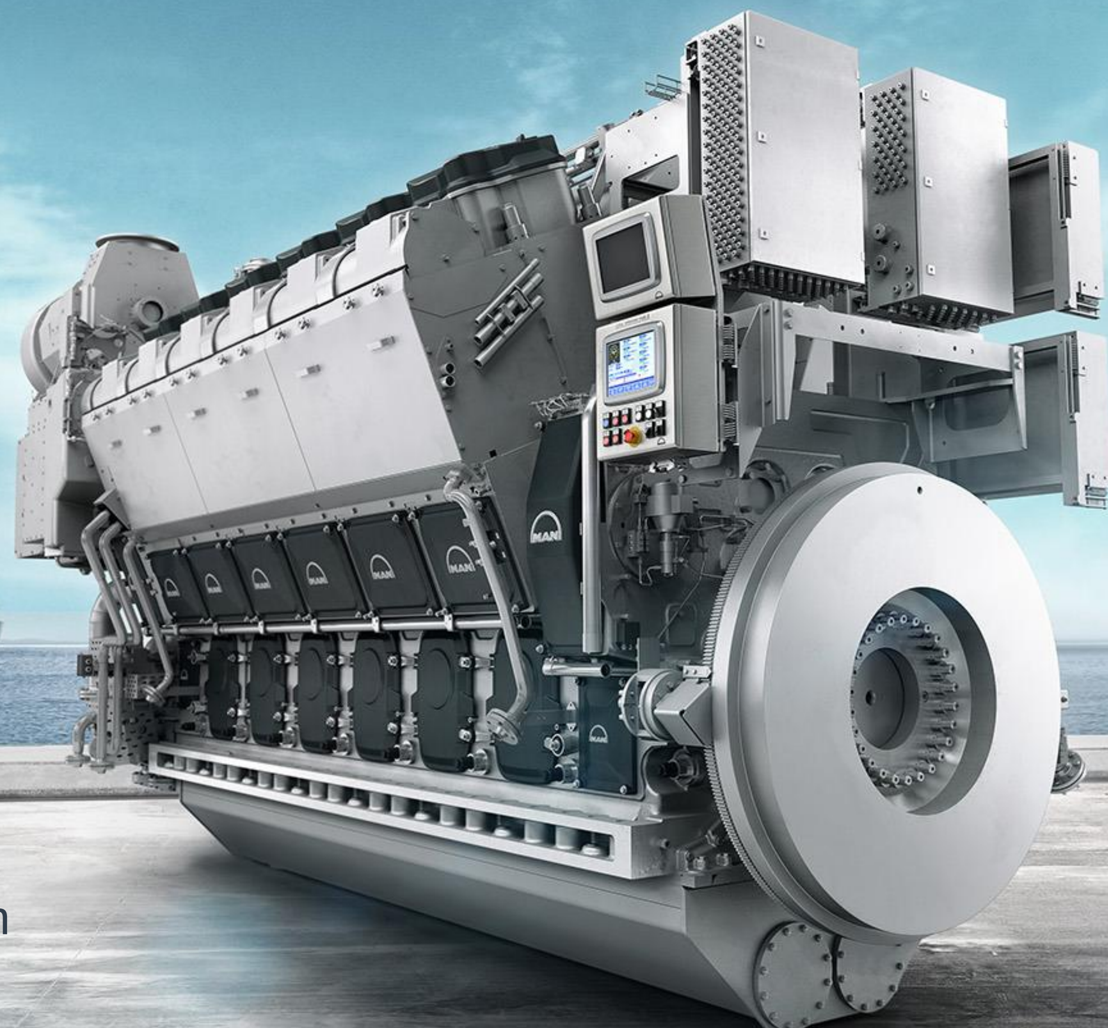
Challenges of Black Carbon determination for marine diesel engines



3rd ICCT Workshop on
Black Carbon

Peter Lauer, 07-08 September 2016

Agenda

1	**Motivation**
2	Methods
3	Results
4	Conclusions
5	Acknowledgements & References

Motivation

Comprehensive characterization of particulate matter (PM) from marine medium speed 4-stroke diesel engines

Evaluation of various measurement methods & instruments to determine

- **Elemental Carbon (EC)**
- **Black Carbon (BC)**
- **Organic Carbon (OC)**

Evaluation & quantification of influence of

- **Different Fuels**
- **Engine Type**
- **Engine Load**

Methods

With focus on EC or BC fraction of PM

PM measurement by MAN Diesel & Turbo (MDT) according to

- **ISO-8178**
- **US-EPA Method-17 (equivalent to ISO-9096 / EN-13284 / VDI-2066)**

Subsequent analysis of PM samples for EC & OC with various methods by

- **DNV-GL**
- **Institut für Gefahrstoff-Forschung** (hazard materials research) **der Bergbau Berufsgenossenschaft an der Ruhr-Universität Bochum**
- **Institute for Applied Environmental Research, Air Pollution Laboratory, Stockholm University**
- **MDT**

Determination of equivalent Black Carbon (eBC) with

- **Filter Smoke Number (FSN) by MDT**
- **Multi Angle Adsorption Photometer (MAAP) by DLR [Petzold]**

Analysis of fuels performed by

- **ASG Analytik-Service Gesellschaft mbH, 86356 Neusäss, Germany**
- **MDT**

Methods

Dilution system for PM according ISO-8178

PM @ 47±5°C after dilution

AVL 472 Smart Sampler Modular GEM140

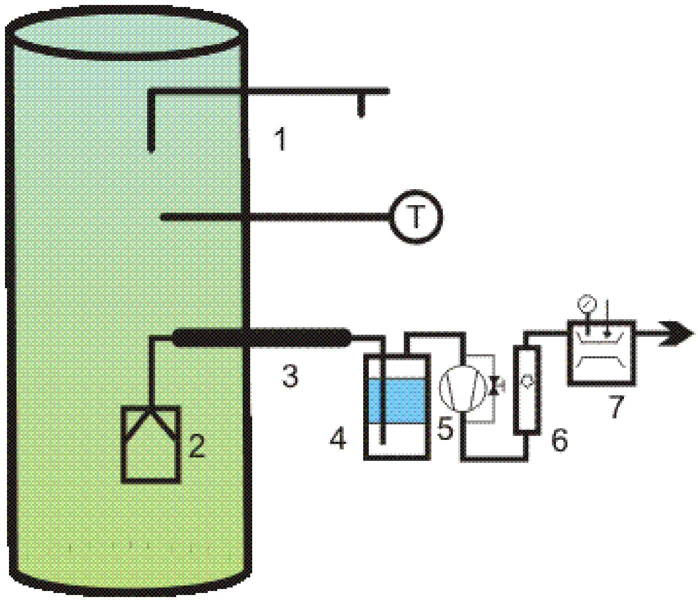
Quartz (Pall QAO 2500) or Teflon (Pall Emfab TX40HI20) fiber filters

Remark:

Particulate measuring according to ISO-8178 is conclusively proven to be effective for fuel sulfur levels up to 0.8% only

Methods

Hot in stack filtration for PM according US-EPA Method-17



PM @ actual exhaust gas temperature in-stack (Dust)

Paul Gothe isokinetic dust sampling system

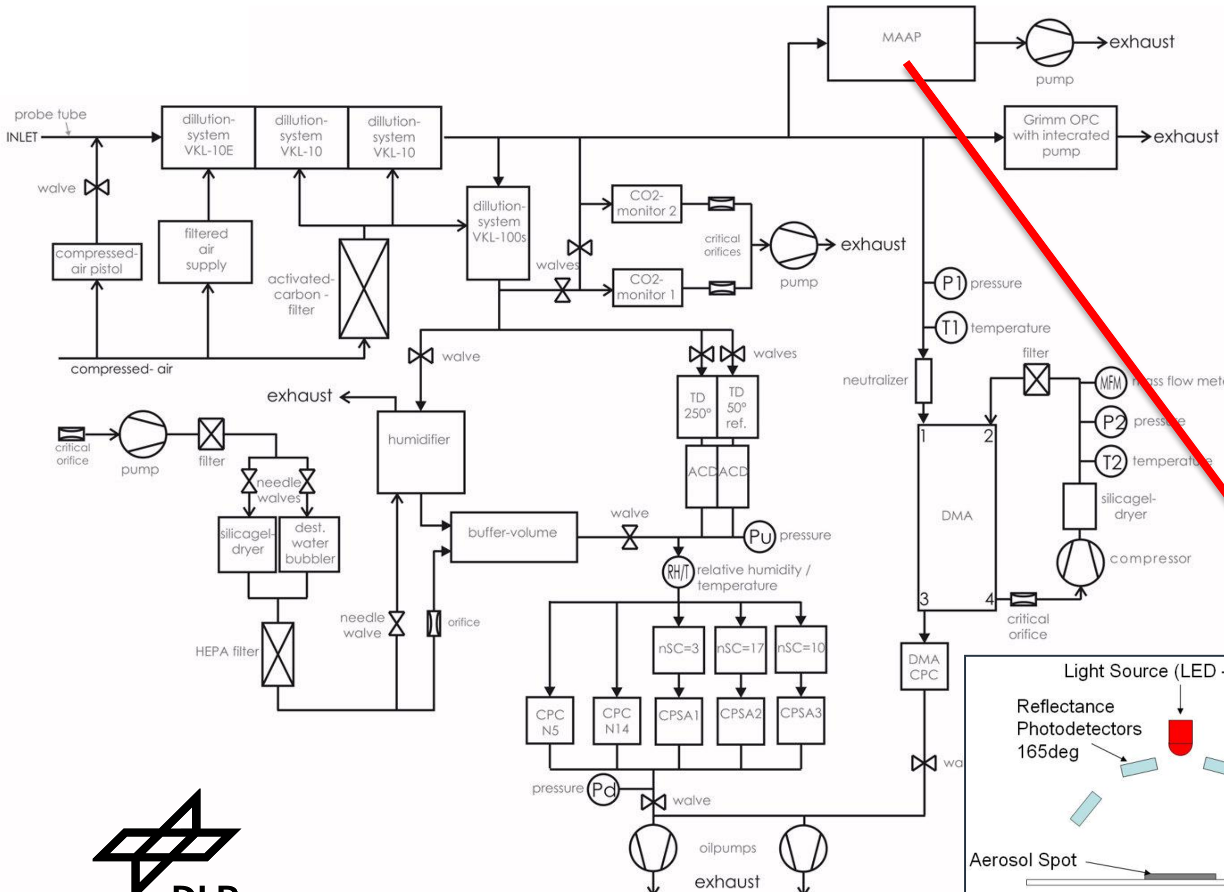
1: Pitot tube
2: Filter device with nozzle
3: Suction tube
4: Drying tower
5: Gas tight pump
6: Flow meter
7: Gas meter

Quartz (Pall QAO 2500) fiber filters

Remark:
Dust measuring according to VDI-2066 is conclusively proven for dry flue gases only

Methods

DLR mobile aerosol measurement system [Petzold]



Thermo Scientific 5012

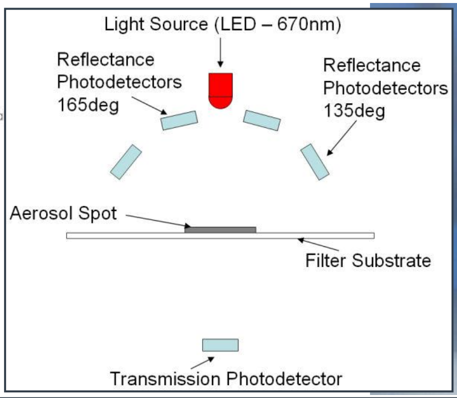
670 nm wavelength

Remark:

For ambient atmosphere, dilution required for direct exhaust gas measurement

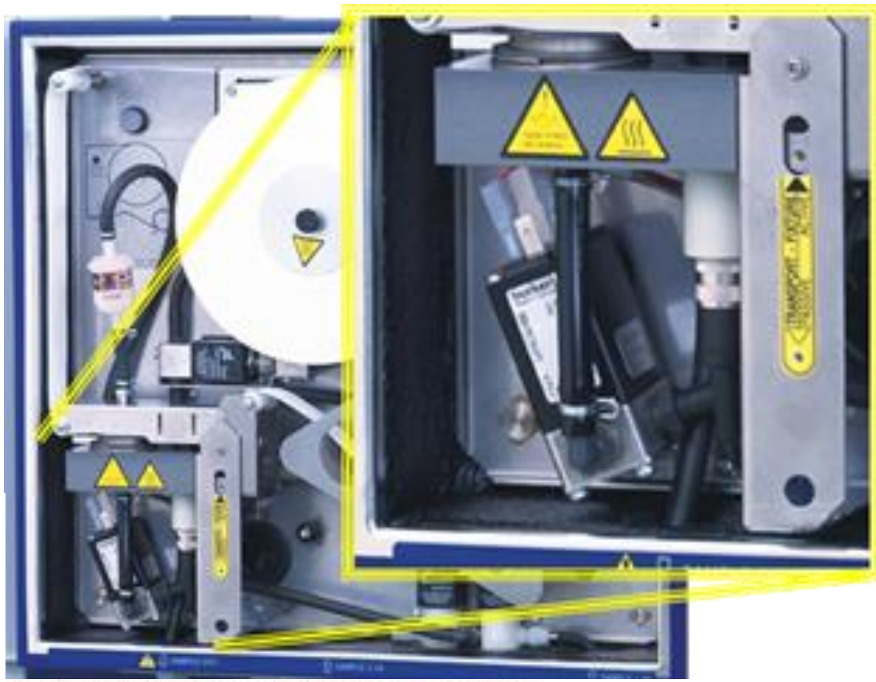
DLR

Institute of Atmospheric Physics



Methods

AVL 415-SE filter smoke number FSN according ISO-10054



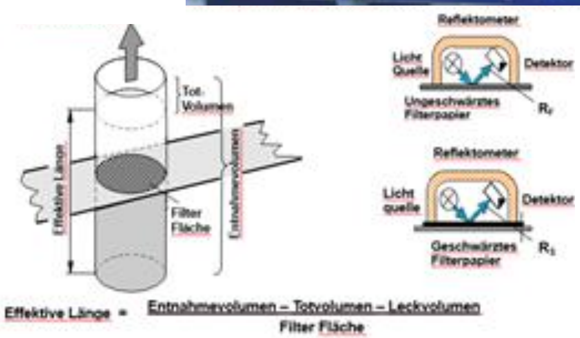
AVL 415-SE

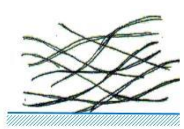
Highest sensitivity @ 550-600 nm wavelength

Remark:

Light scattering is of no influence due to reflection of scattered light from white reflection plate identical to clean filter,

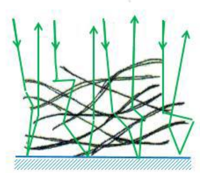
operates on undiluted exhaust gas





FSN Filter paper with

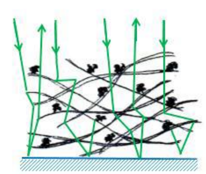
White value plate



Multiple light reflection and refraction

in the

empty FSN filter



Light reflection and adsoption in the loaded FSN Filter paper

Light scattered by the particles is re-directed equivalently to the incoming light

Methods

EC / OC analyzing methods

Coulometric methods from PM or Dust sample:

BGI 505-44:	**Thermodesorption of OC @ 500°C in N_2, subsequent thermodesorption of EC @ 650-800°C in O_2**
VDI-2465-1:	**filter-split, ½ filter: Thermodesorption of TC @ 650°C in O_2**
	½ filter: Toluene-Propanol extraction & thermodesorption of OC @ 500°C in N_2, subsequent thermodesorption of EC @ 650°C in O_2
NIOSH-5040:	**multi-stage thermo-optical method**
VDI-2465-2:	**Thermodesorption of OC @ 80-620°C in He, subsequent thermodesorption of EC @ 300-700°C in O_2**
DNV-GL in-house:	**Improved VDI-2465-2 after extraction & thermodesorption of OC @ 700°C & subsequent EC @ 850°C, see also [IMO PPR 1/8/4]**

Optical methods:

AVL-415 /-S/-SE:	**Filter Smoke Number (FSN)**
	heated: eBC [mg/m³] = 1 / 0.405 x 5.32 x FSN x e $^{0.3062 \times FSN}$
	unheated: eBC [mg/m³] = 1 / 0.405 x 4.95 x FSN x e $^{0.38 \times FSN}$
Thermo-5012:	**Multi Angle Absorption Photometer (MAAP) for ambient atmospheric BC**

Methods

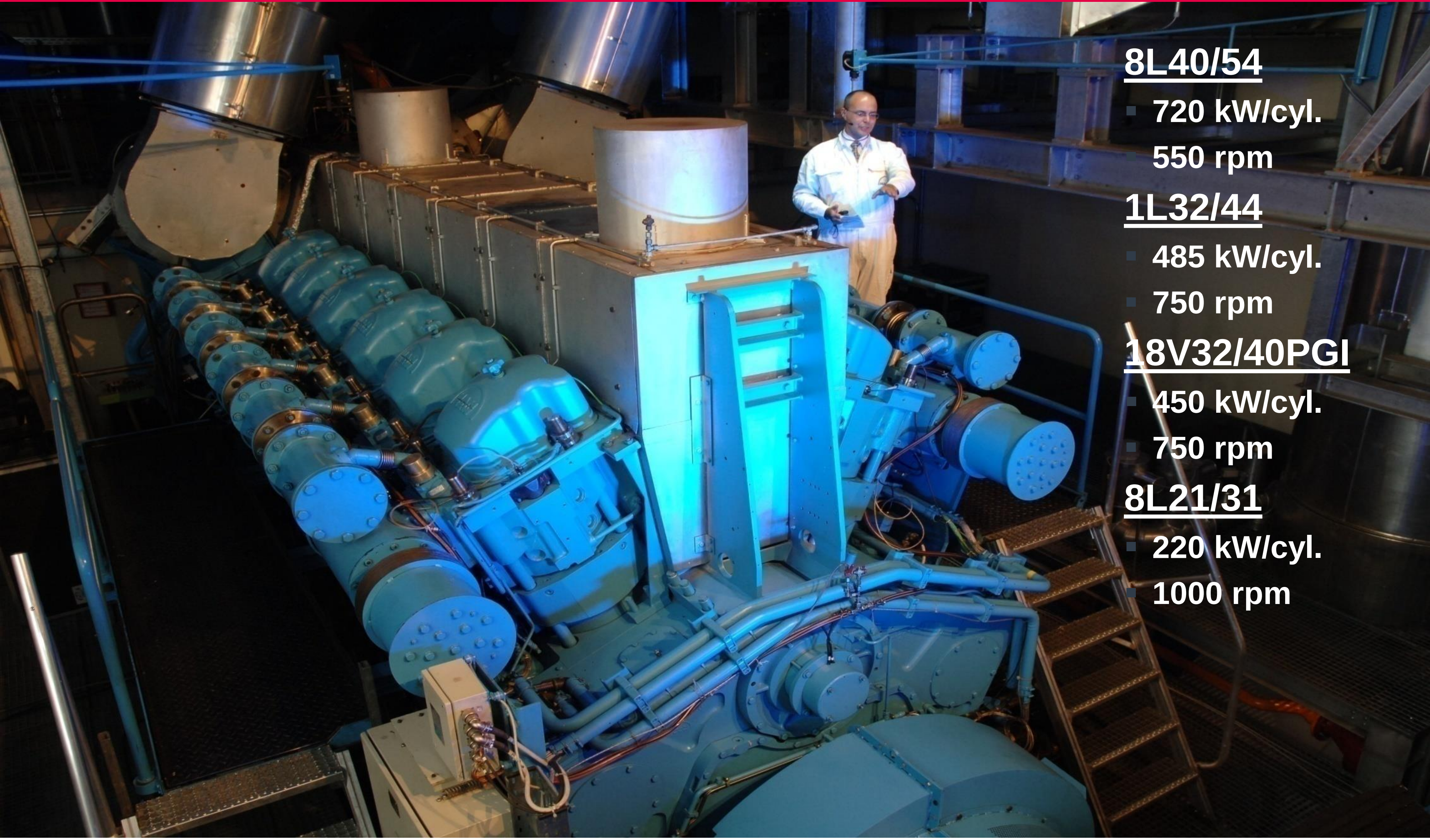
Fuel properties

Fuel	Marine Diesel Oil (MDO)	Palm Oil	Animal Fat	Heavy Fuel Oil (HFO)	Marine Gas Oil (MGO)	EN-590	Natural Gas
Test engine	**8L40/54**	**1L32/44**	**1L32/44**	**1L32/44**	**1L32/44**	**8L21/31**	**18V32/40PGI**
Category	**Distillate**	**Renewable**	**Renewable**	**Residue**	**Distillate**	**Distillate**	**H-Gas**
Type / origin	**DM-B grade**	**Vegetable**	**Animal**	**RM grade**	**DM-A grade**	**ULSD**	**Russian**
Viscosity [mm²/s]	**6.2 @ 40°C**	**29 @ 50°C**	**31 @ 50°C**	**719 @ 50°C**	**2.6 @ 40°C**	**2.7@40°C**	**-**
Density @ 15 °C [kg/m³]	**879**	**916**	**914**	**982**	**838**	**838**	**0.73**
Hydrogen [% mass]	**12.22**	**11.00**	**11.20**	**10.45**	**12.72**	**14.2**	**98.1% Methane**
Carbon [% mass]	**85.53**	**77.30**	**77.00**	**86.94**	**87.08**	**85.3**	**0.02% CO_2**
Sulfur [% mass]	**2.15**	**7.2 ppm**	**2.8 ppm**	**2.17**	**<0.1**	**10.9 ppm**	**10 ppm *)**
Nitrogen [% mass]	**0.10**	**-**	**-**	**0.42**	**<0.1**	**-**	**0.84%**
Oxygen [% mass]	**-**	**11.50**	**11.60**	**-**	**-**	**-**	**-**
Ash [% mass]	**0.01**	**0.0016**	**0.0017**	**0.017**	**0.0011**	**<0.005**	**-**
PAH [% mass]	**12.4**	**-**	**-**	**-**	**-**	**2.6**	**-**
Lower Heat Value [kJ/kg]	**42,077**	**37,144**	**37,292**	**40,435**	**42,966**	**42,692**	**49,266**
Wobbe Index [kWh/Nm³]	**-**	**-**	**-**	**-**	**-**	**-**	**14.74**
Methane number [-]	**-**	**-**	**-**	**-**	**-**	**-**	**93**

Note: *) 20 mg/m³ odorant C_4H_8S Tetrahydrothiophene (THT)

Methods

Test engines



8L40/54
- 720 kW/cyl.
- 550 rpm

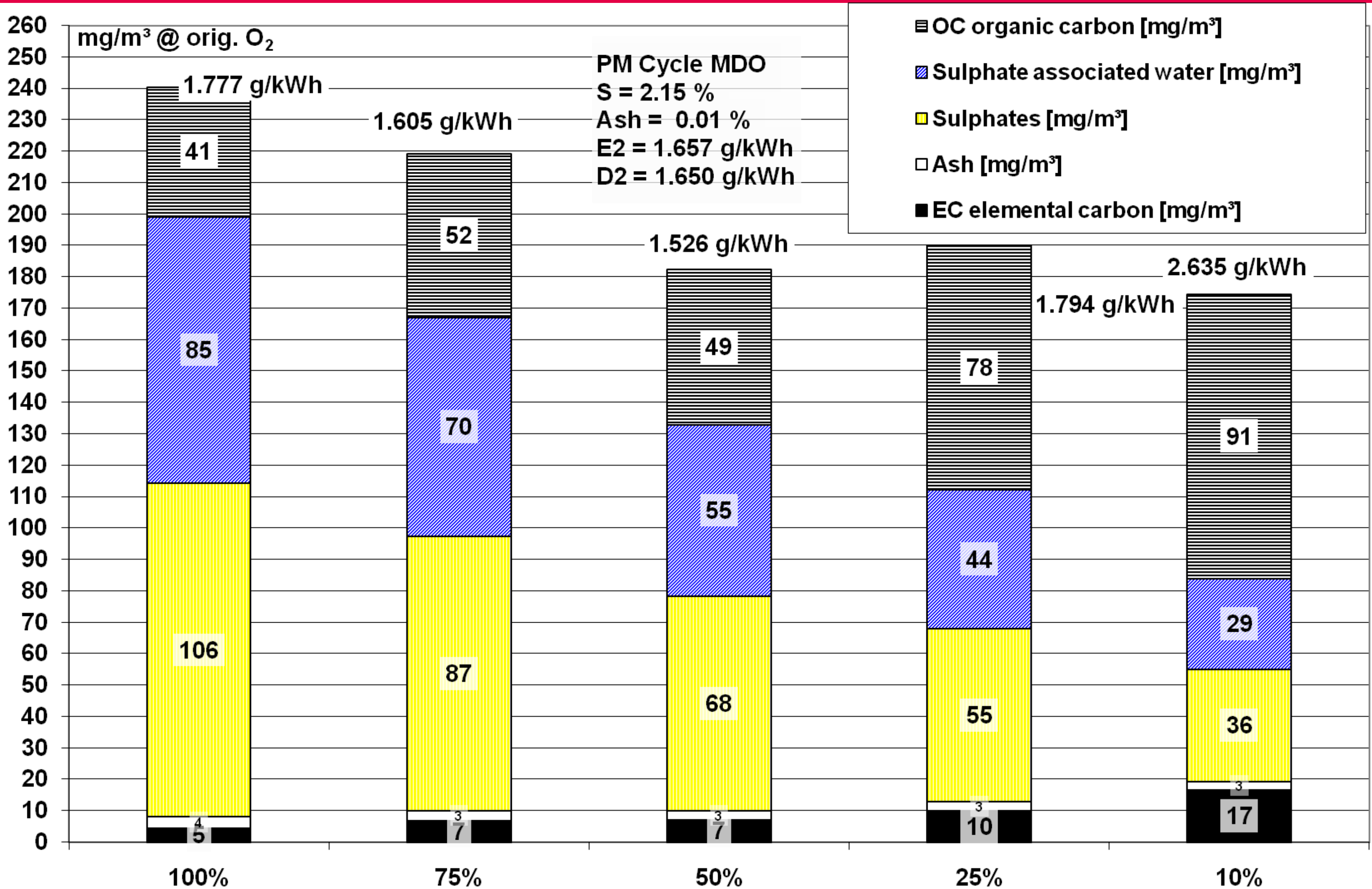
1L32/44
- 485 kW/cyl.
- 750 rpm

18V32/40PGI
- 450 kW/cyl.
- 750 rpm

8L21/31
- 220 kW/cyl.
- 1000 rpm

Results

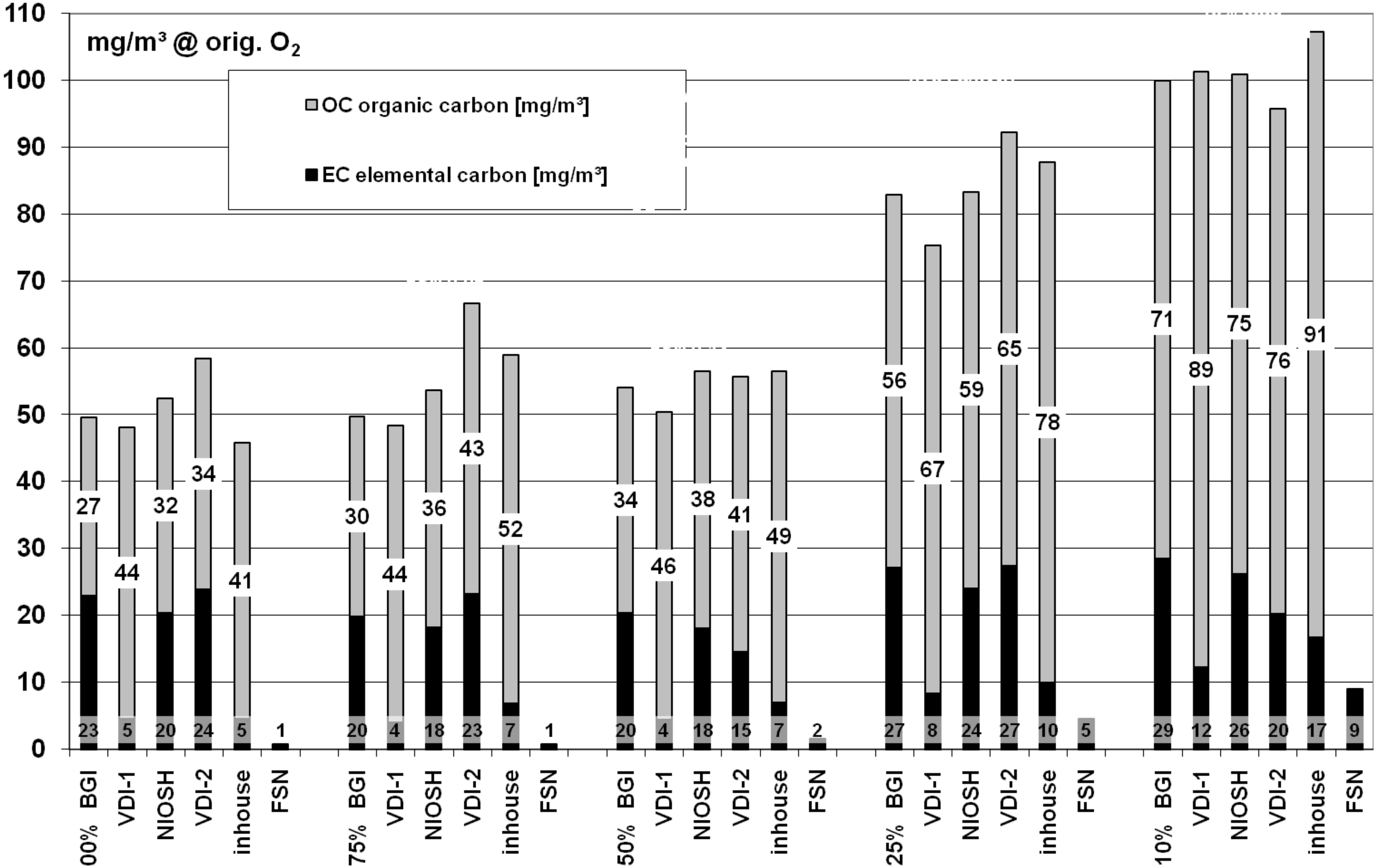
PM emission & composition 40/54 test engine MDO



-> PM consist mainly of sulfates, bound water & organic carbon

Results

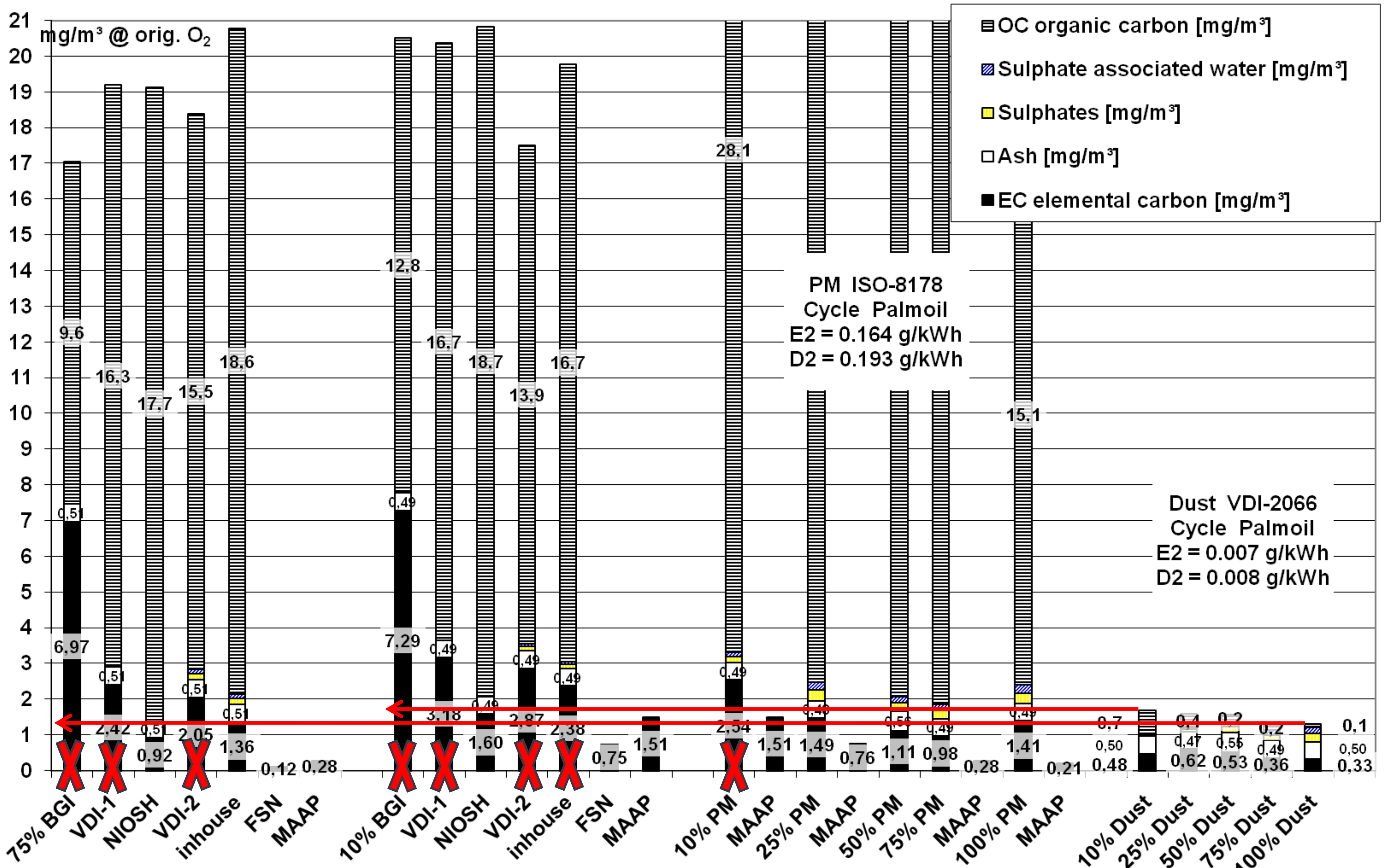
EC/OC results for various analytical methods 40/54 MDO



-> Large differences between methods
Note: NIOSH with manual OC-EC split

Results

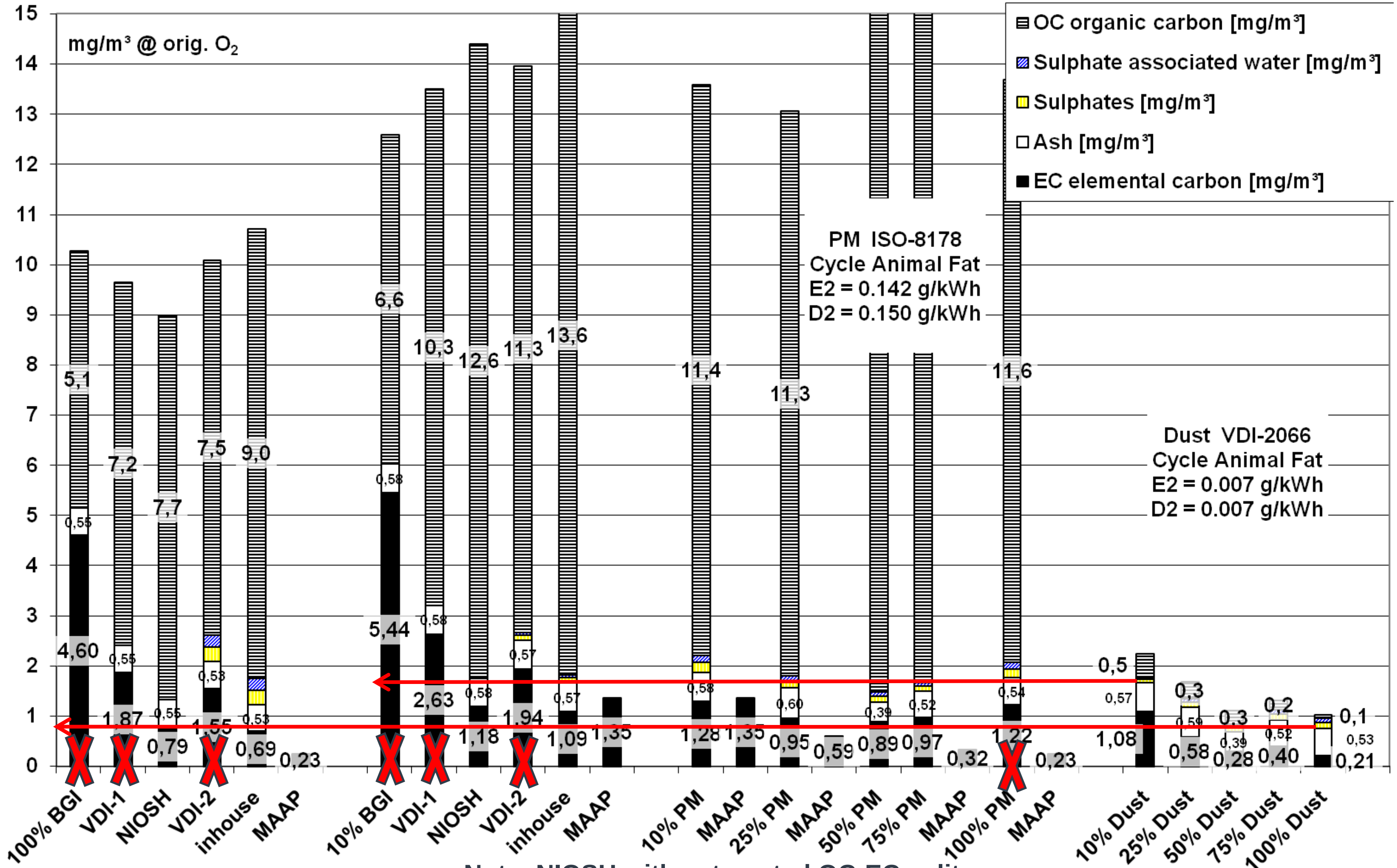
Excluding methods by cross-referencing 32/44 palm oil



Note: NIOSH with automated OC-EC split

Results

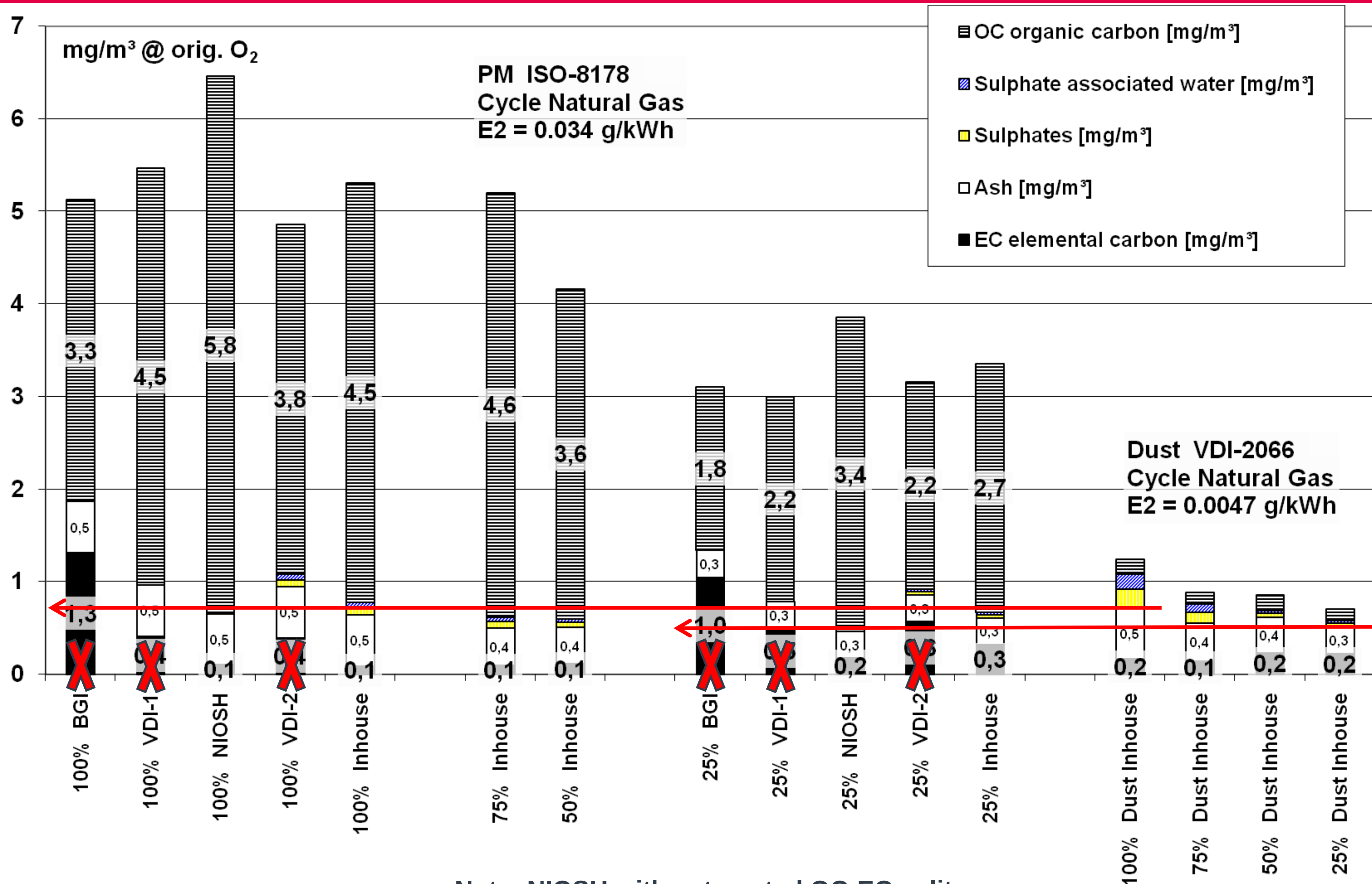
Excluding methods by cross-referencing 32/44 animal fat



Note: NIOSH with automated OC-EC split

Results

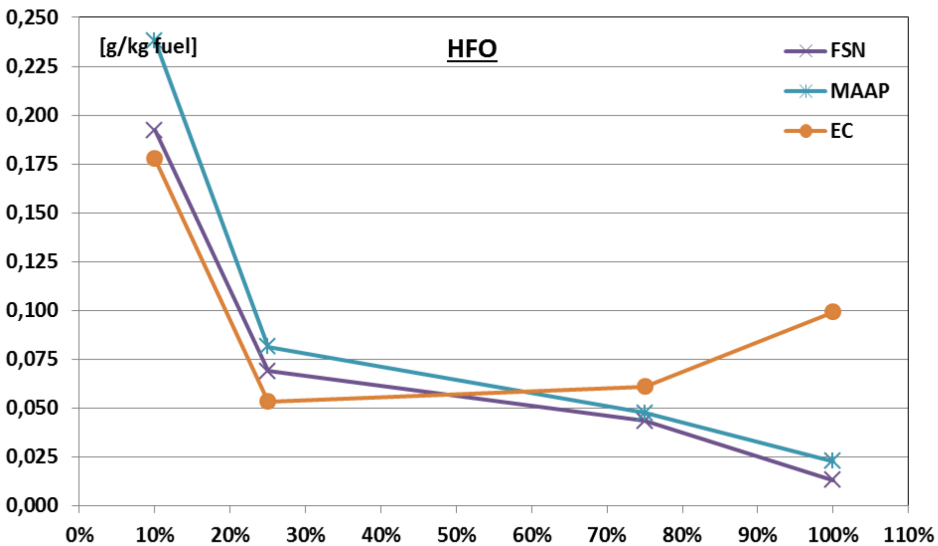
Excluding methods by cross-referencing 32/40PGI Gas

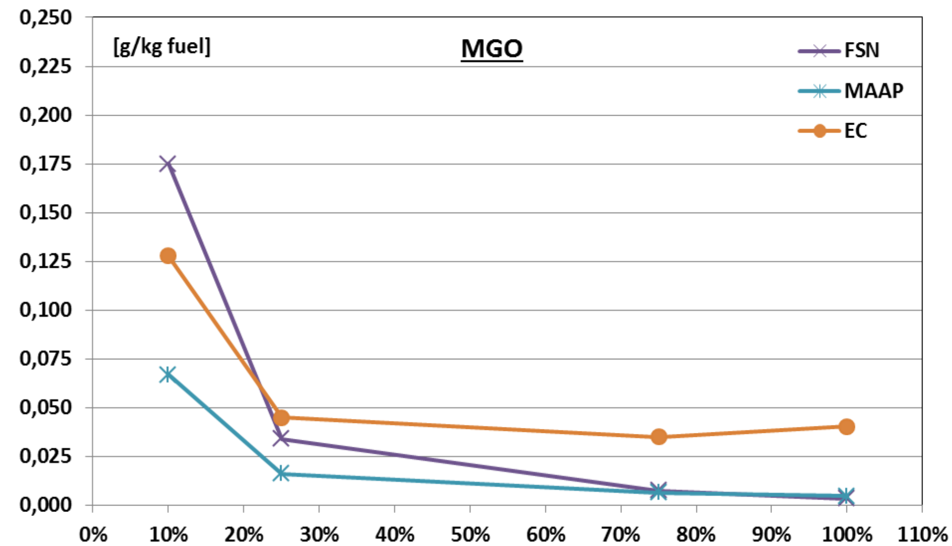


Note: NIOSH with automated OC-EC split

Results

Range of emission factors FSN vs. MAAP vs. EC, 32/44





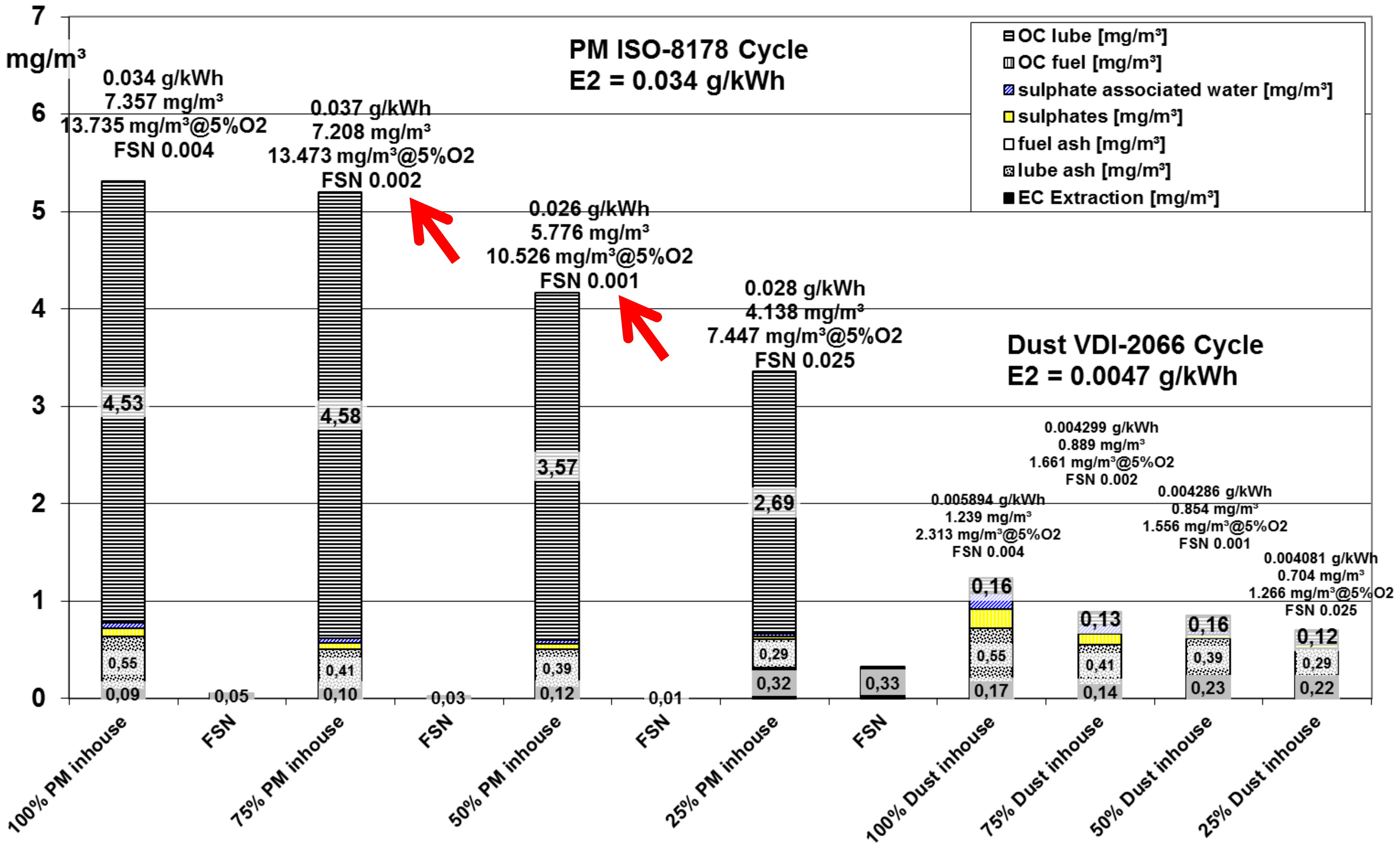
Resulting BC emission factor for medium speed 32/44 diesel engine, mean ±standard deviation of all FSN & MAAP & in-house EC for HFO & MGO, is <u>0.069±0.065</u> (24 points)

-> Is such a single value of any significance?

BC emission factors for fossil fuels in this study <u>do not correspond</u> to values given in [Lack] for slow 0.41±0.27, medium <u>0.97±0.66</u>, and high 0.36±0.23 speed diesel engines

Results

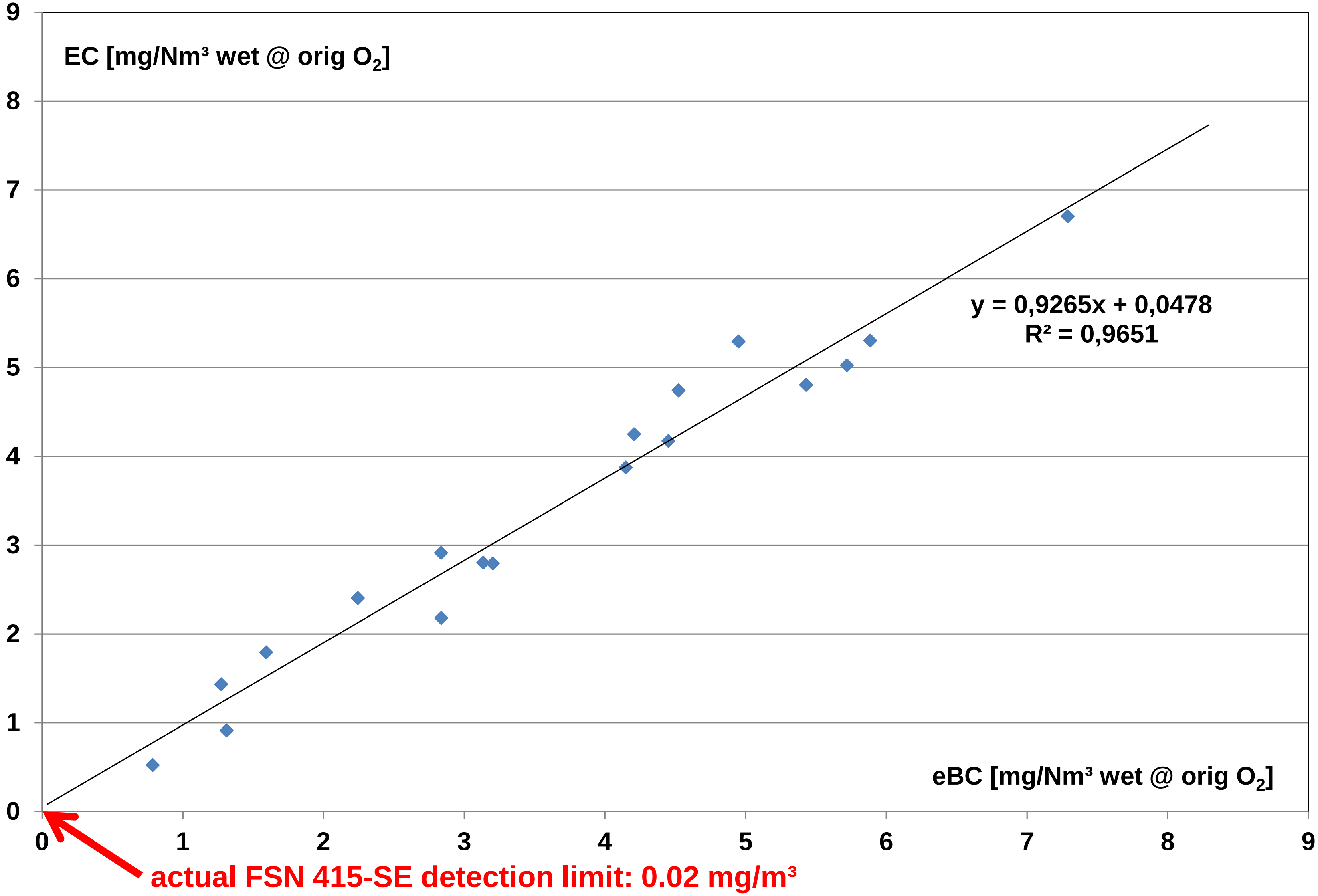
Reaching 415-SE lowest detection limit with 32/40PGI Gas



Note: Measurement time for PM & dust samples 1.5 hours vs. 2 min for FSN !

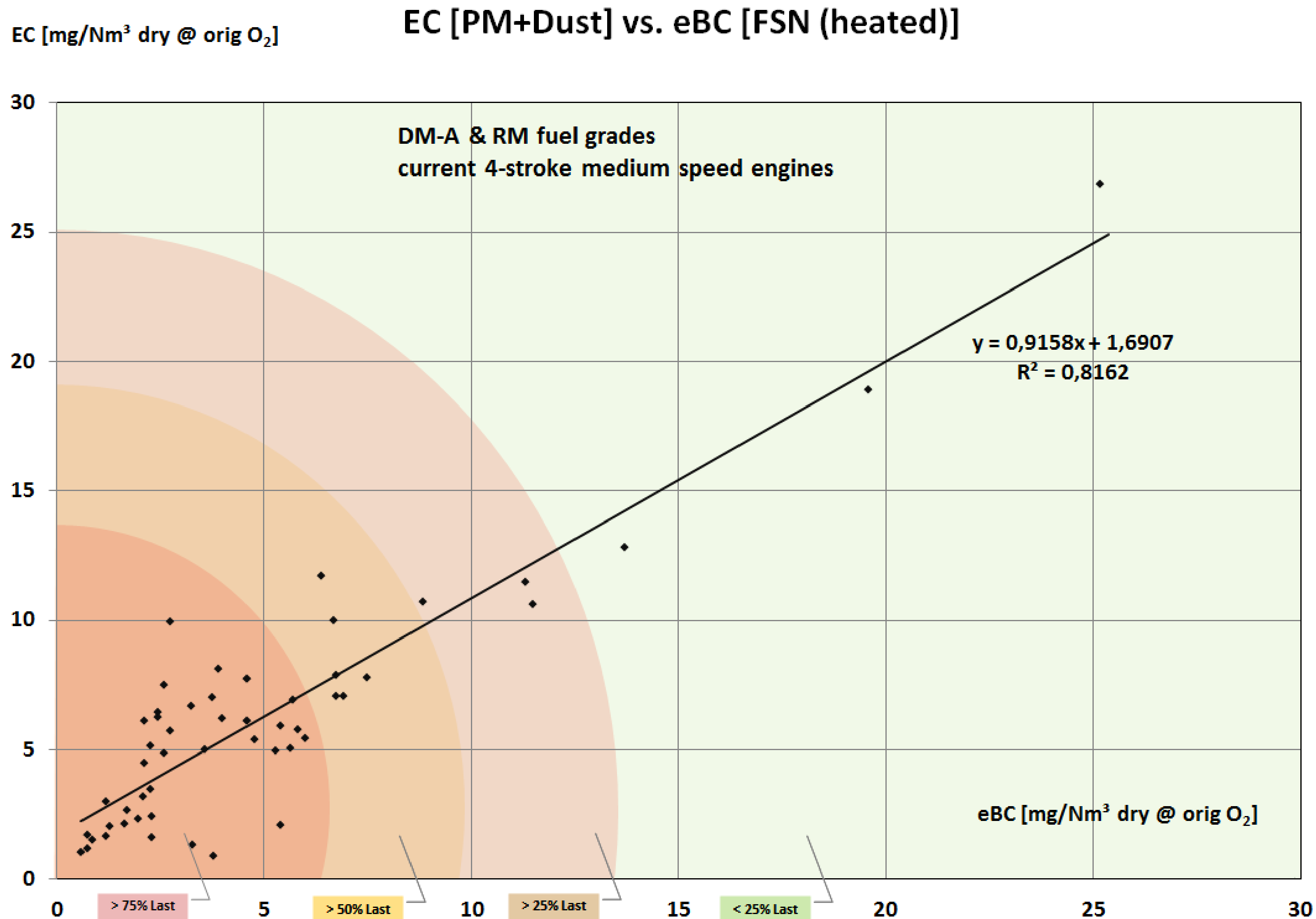
Results

Correlation example EC (PM) vs. eBC (FSN) 21/31 EN-590 ULSD



Results

Correlation example from [PPR 1/8/3] DM-A & RM grade



Conclusions 1/2

Measurement methods, engines & fuels

Analytical methods for determination of total carbon (TC) differ within approx. 25%

But analytical methods can significantly differ up to 200% for OC & EC up to 600%

Contrary to its definition, hot in-stack PM (dust) still contains significant volatile fractions

Almost all thermal methods are prone to charring effects resulting in overestimated EC

Only by cross-referencing, accurate methods can be distinguished

FSN, MAAP, NIOSH & DNV-GL in-house indicate accurate eBC respectively EC values

Although scatter band increase (or precision decrease?) with lower fuel quality, correlations between FSN, MAAP, NIOSH & EC can be established

FSN is sensitive enough even for very low BC emissions

Conclusions 2/2

Measurement methods, engines & fuels

Compared to any other method, which requires either controlled high dilution or additional thermo-chemical analysis, FSN emerged as most robust & sufficiently accurate method

Nevertheless, difference between methods & scatter within a single method persist
-> <u>Why should this improve with PAS?</u>

One order of magnitude difference between MDT values compared to [Lack]
-> <u>What would constitute a reliable data basis?</u>

Contrary to automotive diesels, PM from large medium speed 4-stroke engines mainly consist of sulfates, sulfur bound water & OC, BC tend to increase with lower engine load

Gas engines EC / eBC originate from lube oil

Due to high fuel oxygen content, renewable fuels show lower EC / eBC

Double bonds & aromatic fuel compounds tend to increase EC / eBC, polyaromatic content of RM-grade fuels may vary between 5 – 50% at least
-> <u>What will happen with expected future hybrid fuels?</u>
-> <u>What constitutes a reliable reference fuel?</u>

Acknowledgements & References

Part of presented data taken from BMBF Project "BioClean", Reducing emissions of climate-active gases & particulates from large Diesel engines for ship propulsion systems & stationary power supply by the application of fuels from renewable sources.

Part of presented data taken from FVV Project "Dieselruß" for an improved carbon determination.

BGI 505-44 (ex ZH 1/120.44): https://www.umwelt-online.de/recht/arbeitss/uvv/bgi/505_44a.htm

NIOSH-5040: https://www.cdc.gov/niosh/docs/2003-154/pdfs/5040.pdf

MAAP-5012: https://www.thermofisher.com/order/catalog/product/MODEL5012

AVL-415-SE: https://www.avl.com/-/avl-smoke-meter

DNV-GL in-house method: IMO PPR 1/8/4 - Proposed measurement method for Black Carbon: Determination of Elemental Carbon from PM Filter Samples, EUROMOT submission.

IMO PPR 1/8/3 - Proposed measurement method for Black Carbon, EUROMOT submission.

Petzold, A.: Institut für Physik der Atmosphäre DLR Oberpfaffenhofen, 82234 Wessling, Germany.

Lack D., et al.: Light absorbing carbon emissions from shipping, Geophysical Research Letters Vol. 35: LI13815, 2008.

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Do you have any more questions?

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