SEA-EFFECTS BC
Black carbon measurements from ship engine when using different marine fuels

ICCT’s 3rd and final Workshop on Marine Black Carbon Emissions: BC Control Strategies
September 7-8, 2016, Vancouver, Canada
Research organisations
• VTT Technical Research Centre of Finland Ltd. (P. Aakko-Saksa, T. Murtonen, H. Vesala, P. Koponen, S. Nyyssönen, K. Lehtoranta, T. Pellikka, J. Lehtomäki),
• Finnish Meteorological Institute, FMI (H. Timonen, K. Teinilä, R. Hillamo)
• Tampere University of Technology, TUT (P. Karjalainen, N. Kuittinen, P. Simonen, T. Rönkkö, J. Keskinen)
• UTU (O-P. Brunila, E. Hämäläinen)

Industrial partners
• Funding from Wärtsilä Finland Oy, HaminaKotka Satama Oy, VG-Shipping Oy, Pegasor Oy, Spectral Engines Oy, Gasmet Technologies Oy, Vopak Oy and Kine Robot Solutions Oy
• Contribution in the experiments: Wärtsilä Finland Oy, VG-Shipping Oy, Pegasor Oy, Spectral Engines Oy and Gasmet Oy

External contributions
• AVL (Austria), Metropolia, UEF, Gasera Oy in the BC measurements

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The SEA-EFFECTS BC project

With the expected rise in commercial shipping **in the Arctic, ship emissions are increasing**. Growing attention is given to **black carbon (BC), which increase global warming and ice melting through deposition to ice and snow**. IMO is evaluating needs for control of BC. SEA-EFFECTS BC aims at **more reliable and unequivocal basis of BC emission evaluation to shipping environment, and towards new options for on-line monitoring techniques**.

**WP1** Black carbon (BC) and on-line measurement techniques
Laboratory tests in September 2015
Evaluation of current methods and update by using fuels with different sulphur contents and biodiesel.

**WP2** BC measurement validation on-board: September 2016
Validation of selected black carbon measurement methods on-board (ship equipped with scrubber)

**WP3** Impact of anticipated emission regulations on business potential
Black carbon measurements using different marine fuels

Päivi Aakko-Saksa, VTT Technical Research Centre of Finland Ltd


Research Gate: https://www.researchgate.net/home
Test matrix

Wärtsilä Vasa 4R32 LN 1.6 MW medium-speed engine at VTT’s engine laboratory.

Two engine loads:
- 75% corresponding to the open sea engine loading conditions
- 25% corresponding to the near-harbor engine loading conditions.

Test fuels:
- Marine Diesel Oil with 0.1% sulphur content: “0.1%S”
- Fuel with 0.5% sulphur content: “0.5%S” (not a distillate)
- Heavy fuel oil: “2.5%S”
- A blend of “biofuel” and distillate in ratio of 30:70: “Bio30”

Engine oil: Shell Argina XL 40 engine oil.
Engine and fuels

Wärtsilä Vasa 4R32 LN E

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
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<tbody>
<tr>
<td>Nominal power, kW</td>
<td>1640</td>
</tr>
<tr>
<td>Number of cylinders</td>
<td>4</td>
</tr>
<tr>
<td>Speed, rpm</td>
<td>750</td>
</tr>
<tr>
<td>Bore/stroke, mm</td>
<td>320/350</td>
</tr>
<tr>
<td>Compression ratio</td>
<td>13.8</td>
</tr>
<tr>
<td>Rotating direction</td>
<td>clockwise</td>
</tr>
<tr>
<td>Firing order</td>
<td>1-3-4-2</td>
</tr>
<tr>
<td>Exhaust valve opens / closes</td>
<td>56 °bbdc / 44 °atdc</td>
</tr>
<tr>
<td>Inlet valve opens / closes</td>
<td>52 °btdc / 28 °abdc</td>
</tr>
<tr>
<td>Injection nozzle opening pressure</td>
<td>520 bar</td>
</tr>
<tr>
<td>Static injection advance</td>
<td>12.3 deg</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fuel characteristic</th>
<th>0.1% S DMB</th>
<th>0.5% S IFO</th>
<th>2.5% S HFO</th>
<th>Bio30</th>
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</thead>
<tbody>
<tr>
<td>Density (15/50 °C), kg/m³</td>
<td>870/-</td>
<td>-906/-</td>
<td>-979/-</td>
<td>866/-</td>
</tr>
<tr>
<td>Viscosity (40/50 °C), mm²/s</td>
<td>4.8/-</td>
<td>-127/-</td>
<td>-</td>
<td>6.7/-</td>
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<tr>
<td>Viscosity (80 °C), mm²/s</td>
<td>-</td>
<td>-</td>
<td>187</td>
<td>-</td>
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<tr>
<td>Carbon residue</td>
<td></td>
<td></td>
<td></td>
<td>2.4</td>
</tr>
<tr>
<td>10 %D, % (m/m)</td>
<td>&lt;0.1</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>100 %, % (m/m)</td>
<td>-</td>
<td>3.7</td>
<td>18.3</td>
<td>-</td>
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<tr>
<td>Hydrogen sulfide, mg/kg</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Water (K-F.), mg/kg</td>
<td>53</td>
<td>-</td>
<td>-</td>
<td>197</td>
</tr>
<tr>
<td>Water, % (V/V)</td>
<td>-</td>
<td>0.22</td>
<td>0.54</td>
<td>-</td>
</tr>
<tr>
<td>Total sediment, % (m/m)</td>
<td>&lt;0.01</td>
<td>0.25</td>
<td>0.37</td>
<td>&lt;0.01</td>
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<tr>
<td>Ash (775 °C), % (m/m)</td>
<td>&lt;0.005</td>
<td>0.038</td>
<td>0.094</td>
<td>&lt;0.005</td>
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<tr>
<td>Flash point, °C</td>
<td>86.5</td>
<td>206.0</td>
<td>103.0</td>
<td>67.5</td>
</tr>
<tr>
<td>Pour point, °C</td>
<td>0</td>
<td>+30</td>
<td>-5</td>
<td>-9</td>
</tr>
<tr>
<td>Cloud point, °C</td>
<td>+3</td>
<td>-</td>
<td>-</td>
<td>-3</td>
</tr>
<tr>
<td>90 % (V/V) recovery, °C</td>
<td>358</td>
<td>-</td>
<td>-334</td>
<td>-</td>
</tr>
<tr>
<td>Cetane Index/Number</td>
<td>49.9/-</td>
<td>-44.5/-</td>
<td>-26.1</td>
<td>46.4/-</td>
</tr>
<tr>
<td>CCAI</td>
<td>-</td>
<td>780</td>
<td>848</td>
<td>-</td>
</tr>
<tr>
<td>Acid number (TAN), mg KOH/g</td>
<td>0.025</td>
<td>0.619</td>
<td>0.776</td>
<td>3.33</td>
</tr>
<tr>
<td>Strong acid number, mg KOH/g</td>
<td>-</td>
<td>-</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>HFRR (lubricity), µm</td>
<td>349</td>
<td>178</td>
<td>154</td>
<td>220</td>
</tr>
<tr>
<td>Copper strip corrosion</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Steel corrosion</td>
<td>1</td>
<td>1</td>
<td>intensive</td>
<td>rust</td>
</tr>
<tr>
<td>Iodine value g I/100g</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>49</td>
</tr>
<tr>
<td>Heating value, lower kJ/kg</td>
<td>42.5</td>
<td>42.1</td>
<td>40.3</td>
<td>40.7</td>
</tr>
</tbody>
</table>
BC measurements

From the IMO’s candidate methods, FSN, PAS and MAAP were covered.

**Smoke Meters. BC based on Filter Smoke Number (FSN).** The relative change in optical reflectance of visible light from a filter.

AVL 415S (VTT)
AVL 415SE (AVL)

**AVL Micro Soot Sensor, photo acoustic method (PAS).**

AVL MSS (AVL)

**Multiangle Absorption Photometer (MAAP).** Relative change in optical transmission as particles are collected and measurement of reflectance of scattered light with multiple detectors.

MAAP 5012 (FMI)

**Aethalometers.** Change in absorption of transmitted light due to continuous collection of aerosol deposit on filter.

MAGEE AE42 (FMI)
MAGEE AE33 (Metropolia)

**EC/OC thermal-optical analysis.** Organic and elemental carbon, in-stack (EN 13284-1) and partial flow dilution (ISO 8178) samples.

Sunset 4L (VTT)

**The Soot Particle Aerosol Mass Spectrometer, SP-AMS.** Quantitative aerosol mass loadings, BC and metal analysis.

SP-AMS (FMI)
Sample treatment and other analyses

**Engine testing, gaseous emissions, PM** with in-stack (EN 13284-1) and partial flow dilution (ISO 8178) sampling

**PM compositional analyses** incl. soluble organic fraction, anions, elements and PAHs

**Dilution system** for MAAP, AEs, SP-AMS and TUT instruments.

**Sample treatment with catalytic strippers (CS) and thermodenuder (TD)**

**Pegasor Particle Sensor (PPS).** Measurement of electrical charge carried by particles.

**In-depth analysis**, e.g. PAM, SMPS, CPC, ELPI+, TUT-HTDMA

VTT

VTT and subcontractors

TUT

Pegasor, TUT

Pegasor

TUT, FMI

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## BC instruments – parameters

<table>
<thead>
<tr>
<th>Dilution ratio</th>
<th>Sample</th>
<th>Range (diluted exhaust)</th>
<th>Detection limit</th>
<th>Time-base</th>
</tr>
</thead>
<tbody>
<tr>
<td>AVL 415S/SE</td>
<td>No dilution</td>
<td>~10 lpm</td>
<td>BC 0-32000 mg/m³</td>
<td>~0.02 mg/m³</td>
</tr>
<tr>
<td>AVL MSS</td>
<td>DR 7 (spec 2-20)</td>
<td>3.8 lpm</td>
<td>BC 1-1000 mg/m³</td>
<td>up to 10 Hz</td>
</tr>
<tr>
<td>MAAP</td>
<td>DR &lt;200; DR &gt;600</td>
<td>6 lpm (spec 16.7 lpm), PM1</td>
<td>BC 0-60, 0-180 µg/m³ (30/10 min 16.7 lpm)</td>
<td>&lt;0.1 µg/m³ (2 min.)</td>
</tr>
<tr>
<td>Aethalometers</td>
<td>DR &lt;200; DR &gt;600</td>
<td>2 lpm. 1 min av. (spec 2-5 lpm) PM1</td>
<td>BC &lt;0.01 to &gt;100 µg/m³</td>
<td>&lt;0.005 µg/m³ (1 hour)</td>
</tr>
<tr>
<td>SP-AMS</td>
<td>DR &lt;200; DR &gt;600</td>
<td>0.1 lpm</td>
<td>BC 0.04 µg - 2 mg/m³</td>
<td>&lt;0.04 µg/m³ (1 min)</td>
</tr>
<tr>
<td>PPS-M</td>
<td>DR 5</td>
<td>&lt;10 lpm</td>
<td>PM 1-250 mg/m³</td>
<td></td>
</tr>
<tr>
<td>EC</td>
<td>a</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**a** ISO 8178 PM sampling: DR 8, in-stack sampling: no dilution

**b** Samples in this study: EC 0.7-16 µg/cm²
Test set-up

Turbo

Exhaust duct Ø 448mm

M3: 590 cm

Muffler

In-stack
OC/EC

Two dilution setups: DR<200 and DR>600

PAM

CO, THC, NOx, CO2

Multi-component FTIR

BC FSN AVL 415S

BC FSN AVL 415SE

BC ISO 8178 DR8 OC/EC
at 3 labs

BC AVL MSS, DR 7

BC AE42

SMPS, CPC ELPI+
TUT-HDTMA

BC MAAP

CS3

PM Pegasor PPS,
DR 5

TD

CS1

CS2

BC AE33

BC SP-AMS

CPC, SMPS
Nano-SMPS

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TUT dilution system
# Daily protocol

| Warm-up | 10 minutes at 50% load  
50 minutes at 75% load. |
| --- | --- |
| **Tests at 75% load (morning session)** | • **In-stack:** in minimum three collections, Munktel MK360 quartz filters  
• **ISO 8178 collections**  
  o Pallflex TX40 filters (primary and back-up): 7-8 collections with 2 sampling systems  
  o Munktel MK360 quartz filters and Pallflex TX40 back-up filters: min. 3 collections  
• **FSN AVL 415S/SE and AVL MSS** sampling periods synchronized with ISO 8178 Microtroll  
• **Real-time instruments** measuring continuously  
• **Periodically ON/OFF:** CS1&TD before AE33 and SP-AMS. CS2 before MAAP. CS3 before PPS. |
| **Load change** | **Stabilisation at least 30 minutes** |
| **Tests at 25% load** | Same procedure as at 75% load |
The best practices for engine emission tests followed

Before/after test campaign
- Engine and test set-up stabilisation before the campaign
- Lube oil running hours checked
- Fuel and lube samples analysed
- One fuel tested before and after campaign (stability of the set-up)

During the test campaign
- Warm-up and load change protocol
- On-line measurements (e.g. NO with FTIR) to follow engine stability
- Fuel temperature adjusted according to engine manufacturer’s requirements

Periodical recordings
- Engine speed, alternator power, rack position, bearing temp, HC of blow-by
- Test cell T&RH, intake air T, pressure diff, under pressure in meas pipe, T and P before/after TC, TC speed, air gauge P before cooler/ in receiver, air T in receiver, exhaust T, cyl. T
- Water T from different locations
- Fuel mass flow rate in/out/booster, fuel T/P after feed pump, fuel P before/after engine (booster), fuel volume flow rate in/out, fuel T before/after engine, fuel viscosity before engine, fuel P on engine (in/out)
- Lub. oil T from different locations, lube oil pressure
High dilution ratios needed for some BC instruments are a source of uncertainty

BC instruments designed for the atmospheric measurements, such as MAAP and aethalometers, require high dilution ratios at high BC concentrations.

Dilution ratio is a multiplier in the calculation of the BC results, and thus uncertainty in DR is directly reflected in the uncertainty of the BC result.

When using high DR and/or pre-treatment (CS, TD), size-dependent corrections for soot particle losses are need for the calculation of the results.

\[
DR = \frac{C_{\text{raw}} - C_{\text{bg}}}{C_{\text{dil}} - C_{\text{bg}}}
\]
High dilution ratios are challenging. How to measure accurately DR >500?

In these measurements
- DR based on CO₂ measurements*) at different locations of the sampling system.
- Water content of exhaust for dry/wet correction (Gasmet FTIR).
- Sampling and dilution air T, RH, impurities (PN) adjusted/monitored.
- Heated ejector diluter (350 °C).

Observations
- When using dried only dilution air, accurate on-line analysis of CO₂ of dilution air is needed due to CO₂ contamination risk in the engine environment.
- Using ultra-pure dilution air without CO₂ is recommended.

*) NOₓ is not feasible for determination of DR due to low diluted NOₓ concentration (e.g. at NOₓ of 1000 ppm and DR 500 → diluted NOₓ 2 ppm)
RESULTS FROM LABORATORY TESTS
Particulate matter PM (ISO 8178, DR8) as mass/Nm³, kilograms of oil equivalent (kgₖₒₑ) and mass/kWh
Share of EC in PM low for all fuels. Heavy PAHs lowest for 0.1%S and Bio30.
Black carbon emission in different units

BC/FSN (mg/Nm³)

BC/FSN (g/kgoe)

Bubble size = mass/kWh

0.5%S
2.5%S
0.1%S
Bio

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Low BC with MAAP at high BC conc. when DR<200

Comparison of methods (DR<200 or no dilution)
...but similar BC level with MAAP and AEs at DR>500.

Note: BC results at DR>500 are not quantitative due to uncertainty in DR.
Hyvärinen et al. (2013) also observed a measurement artifact in the MAAP at high BC concentrations. The averaging procedure of the photodetector raw signals. It was found that, in addition to the erroneous temporal response of the data, concentrations higher than 9 μg m⁻³ (at the flow rate of 16.7 L min⁻¹) are underestimated by the MAAP. The underestimation increases with increasing BC accumulation rate. At a flow rate of 16.7 L min⁻¹ and concentration of about 24 μg m⁻³ (BC accumulation rate ~ 0.4 μg min⁻¹), the underestimation is about 30 %. There are two ways of overcoming the MAAP artifact. One method is by logging the raw concentrations higher than 9 μg m⁻³ (at the flow rate of 16.7 L min⁻¹) are underestimated by the MAAP. The underestimation increases with increasing BC accumulation rate. At a flow rate of 16.7 L min⁻¹ and concentration of about 24 μg m⁻³ (BC accumulation rate ~ 0.4 μg min⁻¹), the underestimation is about 30 %. There are two ways of overcoming the MAAP artifact. One method is by logging the raw

In Hyvärinen et al. MAAP underestimated BC by 30 % when mass accumulation rate exceeded 0.4 μg min⁻¹, which is equivalent to BC concentration of 24 μg m⁻³ at flow rate of 16.7 lpm (1 m³ h⁻¹). In our tests, MAAP flow rate was 6 lpm -> BC mass accumulation rate of 0.4 μg min⁻¹ was reached at BC concentration of 67 μg m⁻³, which was exceeded with 0.1%S and 0.5%S fuels at 25% engine load using DR<200.
Minimum DRs needed for MAAP

DR needed for MAAP at 6 lpm

DR needed for MAAP at 16.7 lpm

BC concentration, raw exhaust (mg/m³)
Findings on the BC measurement methods

Comparability was relatively good between the BC results obtained with two smoke meters, AVL MSS (PAS), aethalometers and MAAP. EC compared relatively well with BC.

High DRs required for MAAP and AEs at high BC concentrations lead to high uncertainty in the BC results (DR is a multiplier in calculation). For high DRs, ultra-pure dilution air w/o CO₂ is needed.

Measurement range of MAAP is particularly narrow. MAAP artifact can occur already at the BC concentration of 10 µg/m³.

Many challenges can be alleviated, if instruments can operate without dilution or at low DR.

CS and TD might alleviate bias between different BC instruments, but at the cost of increased complexity of the test set-up. When using high DR and/or pre-treatment (CS, TD), size-dependent corrections for soot particle losses are need for the calculation of the results.

With high-sulphur fuels, clogging and corrosion related problems are threats.
Findings on the BC control

The BC emission was dependent on engine load. **The BC emission was substantially higher at 25% load than at 75% load.**

**75% load:**
- The highest BC emission for the 2.5%S fuel, while the BC emission from the 0.5%S, 0.1%S and Bio30 fuels were lower.
- At the high load combustion temperature is high and combustion more complete even with asphaltene fuels than at lower loads.

**25% load:**
- The highest BC emission for the 0.5%S fuel. Presence of BC precursors in fuel depends on crude oil and processing technology.
- The 2.5%S fuel, showed lower BC emissions than the 0.5%S fuel presumably as some metal oxides catalytically enhance combustion.
- The BC emissions for the 0.1%S and Bio30 fuels were also lower than those for the 0.5%S fuel.
- The lowest BC emission was observed for the Bio30 fuel presumably basing on its oxygen content.
Summary

Different instruments rated the BC emissions in the same order despite of their different measurement principles. Challenges with high dilution ratios needed for the BC instruments designed for the atmospheric measurements (MAAP, AEs) can be alleviated, if instruments can operate without dilution or at low DR.

The results unveiled dependences between the BC emissions, fuels and loads for the engine studied, and how different BC measurement methods reflected changes in BC emissions. For example, reduced sulphur content of the fuel efficiently reduced the PM emission, but not necessarily the BC emission. BC was not directly dependent on the fuel sulphur content.

Measurements continue on-board a ship equipped with scrubber in September 2016.