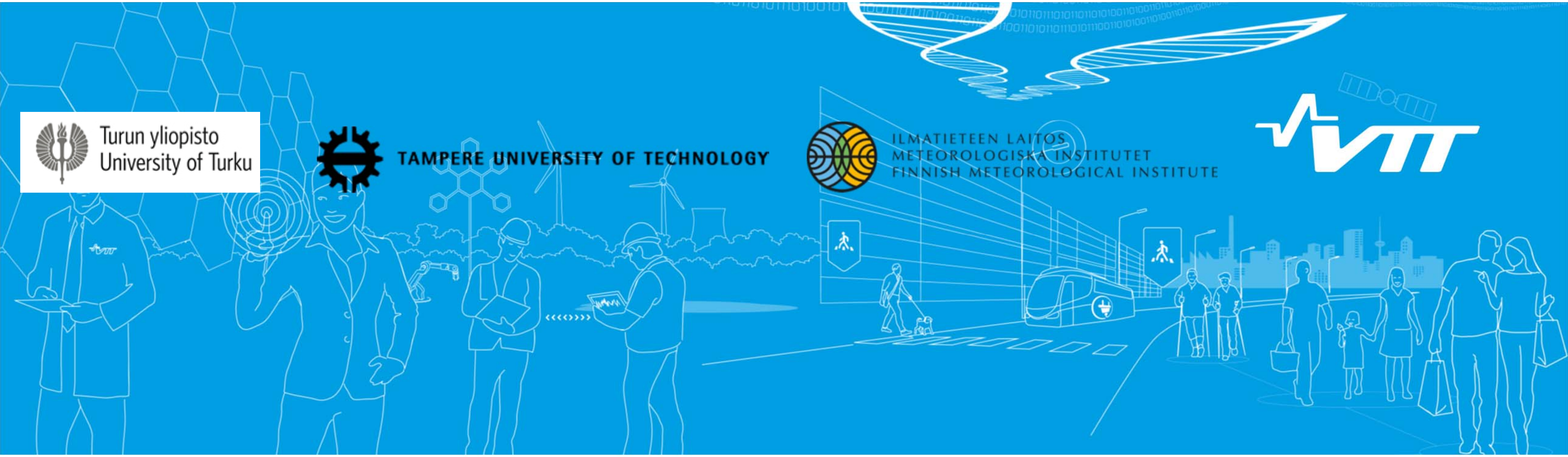

SEA-EFFECTS BC 2015-2016

Tekes Arctic seas program

Black carbon results from Finland (SEA-EFFECTS BC project)

ICCT 4th BC Workshop on Marine BC
4-5 October, 2017, Washington DC

List of authors in the next slide.

SEA-EFFECTS BC project, Finland, 2015-2016

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Industrial partners

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External contributions

- AVL (Austria), Neste, Metropolia, UEF, Gasera Oy in the BC measurements

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Content

1. BC results from **laboratory (WP1)** *)**) and **from ship (WP2)** ***)
2. Challenges in the BC measurements**)
3. Challenges in the EC measurements
4. Uncertainty
5. Summary

Reports and articles: *http://www.vtt.fi/sites/sea-effects*

**) CIMAC Paper no. 068, 6-10 June 2016, Helsinki, Finland. (laboratory WP1).*
***) Aakko-Saksa et al. Research report VTT-R-02075-17 (laboratory WP1)..*
****) Timonen et al. Research report VTT-R-04493-17 (on-board WP2).*

A part of the results from WP1 (laboratory tests) reported to IMO PPR 4


VTT
BC RESULTS

Test matrix in laboratory (WP1)

Wärtsilä Vasa 4R32 LN 1.6 MW

medium-speed engine at VTT's laboratory.

Two engine loads:

- 75% (open sea loading).
- 25% (near-harbor loading).

Test fuels:

- Marine Diesel Oil with 0.1% sulphur content: "0.1%S"
- 0.5% sulphur ful: "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.

Test matrix on-board a modern cruising ship (WP2)

Two different engine sizes

- ME1 and ME2

Two engine loads:

- 40% and 75% engine loads

Two different fuels:

- HFO fuel
- MGO fuel (only ME2 at 40% load)

Scrubber and SCR measurements

- Before/after scrubber for ME1 and ME2
- Limited measurements before/after SCR for ME2

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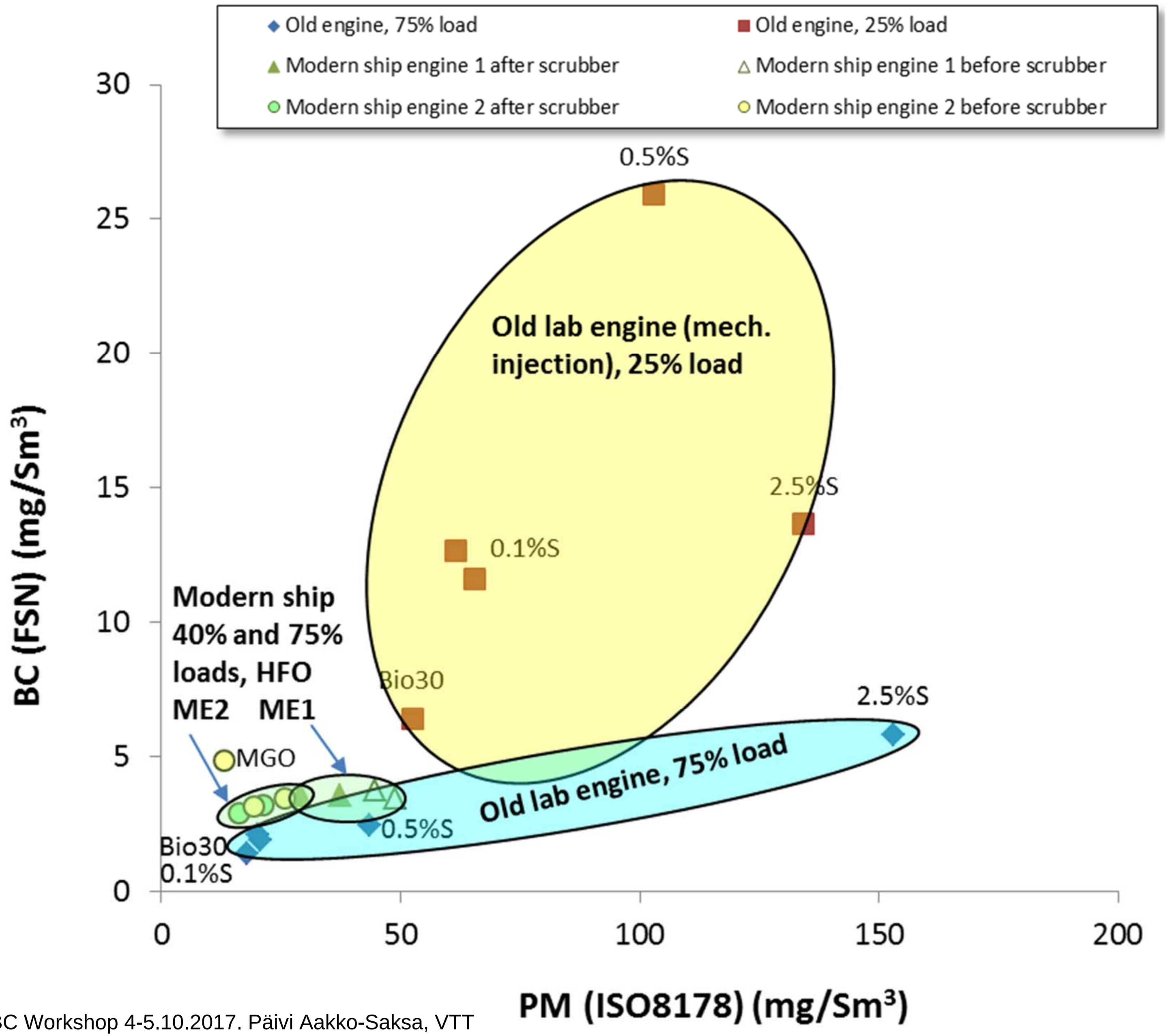
PM and BC from an old engine in lab and from a modern ship



Laboratory engine (WP1):
** CIMAC Paper no. 068, 2016.*
* Aakko-Saksa et al. Research report VTT-R-02075-17 (www.vtt.fi in 9/2017).

On-board a ship (WP2):
** Timonen et al. Research report VTT-R-04493-17 (www.vtt.fi in 9/2017).*

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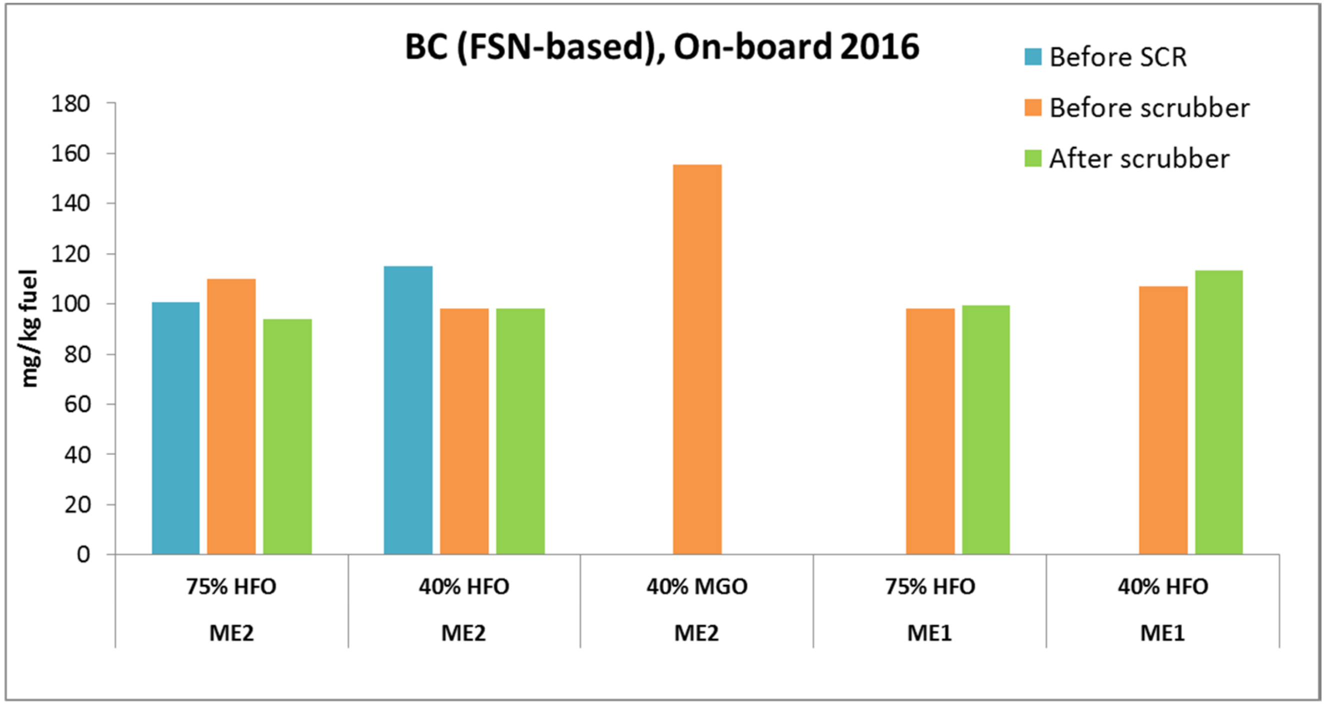
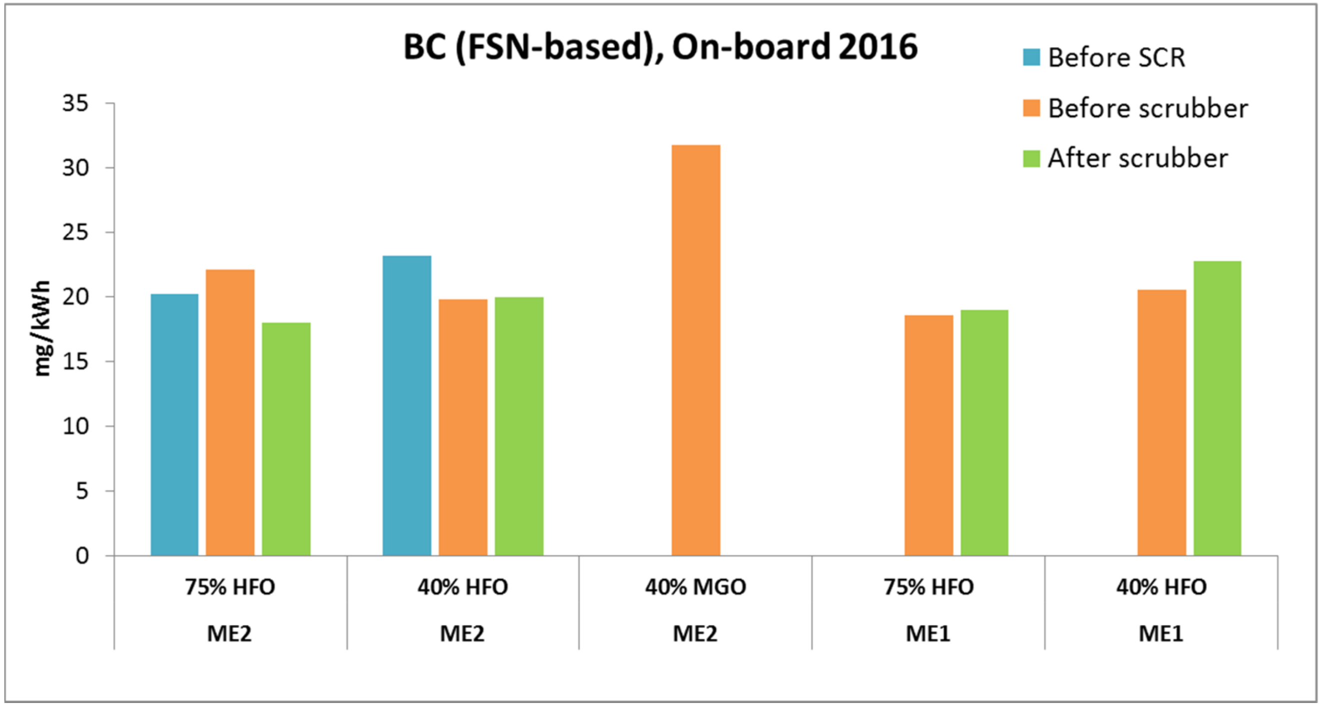
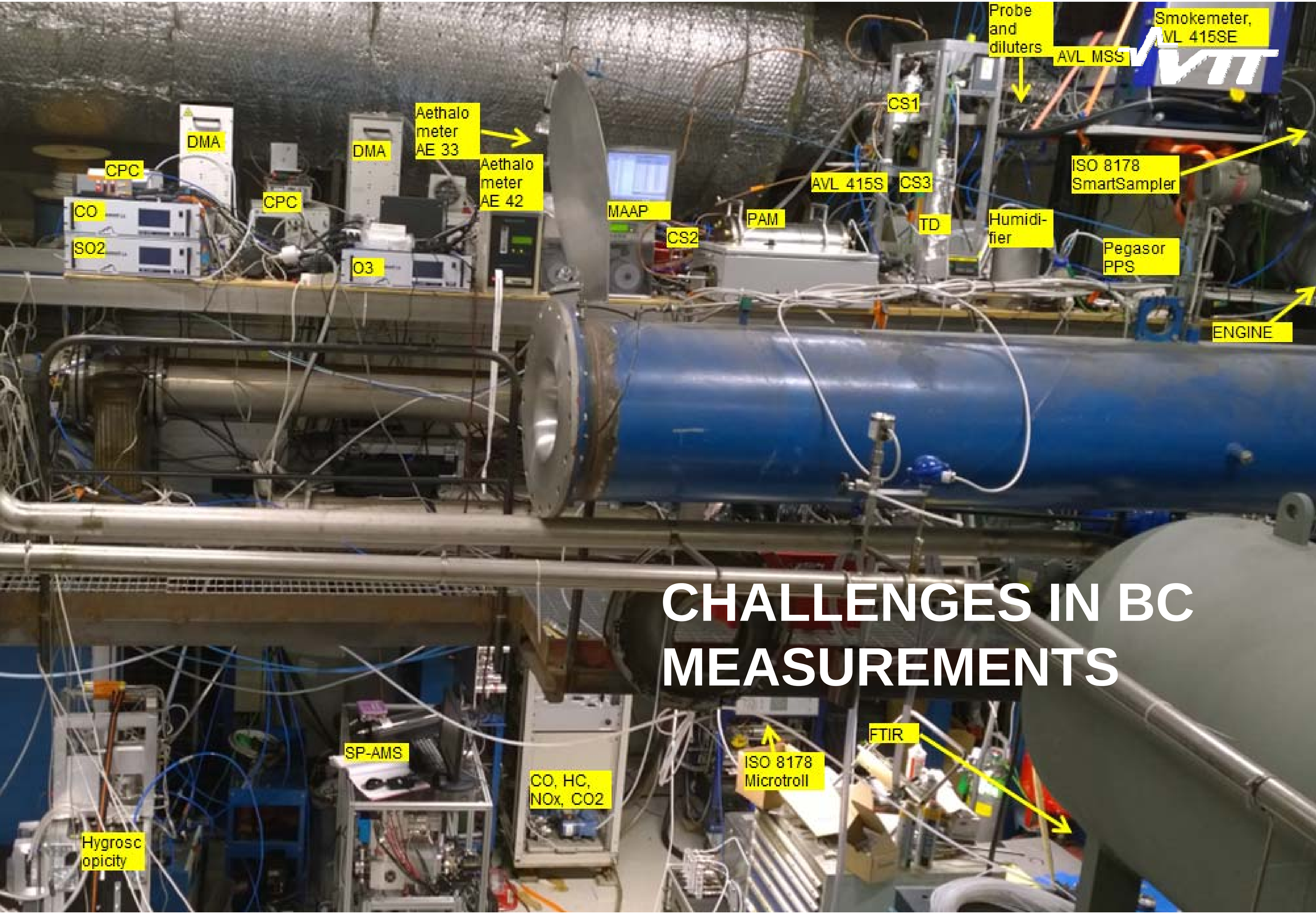




BC on-board a modern ship

- No significant differences in BC before/after scrubber
- Also SCR did not affect BC significantly.

CHALLENGES IN BC MEASUREMENTS

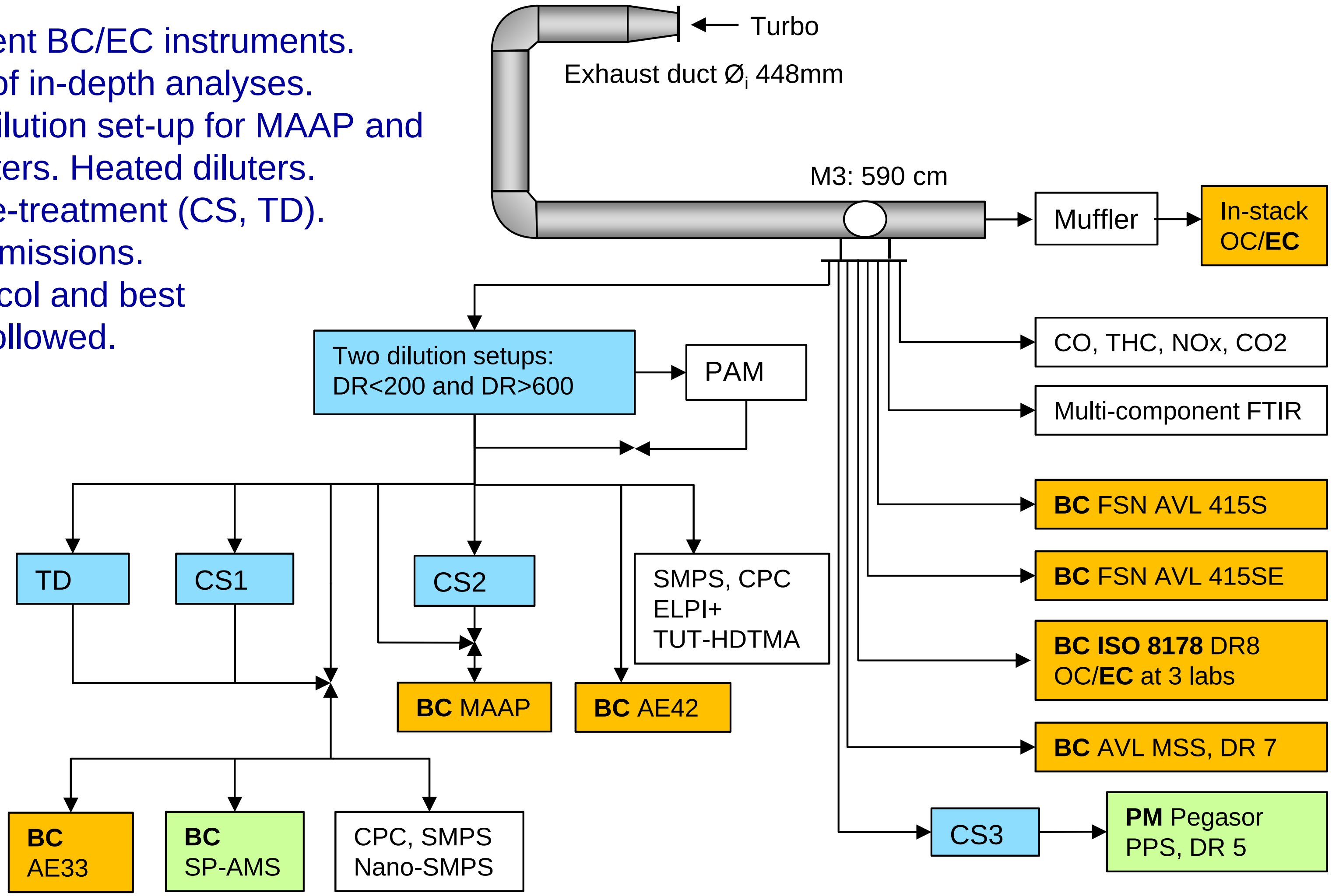


From the IMO's candidate BC methods, FSN, PAS and MAAP were included

BC: 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)*
BC: AVL Micro Soot Sensor, photo acoustic method (PAS).	AVL MSS (AVL)
BC: 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)*
BC: 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, partial flow dilution (ISO 8178) samples (in-stack EN 13284-1 in lab)	Sunset 4L *(VTT)*
The Soot Particle Aerosol Mass Spectrometer, SP-AMS. Chemical composition (ions, organics, BC, metals) of submicron PM	SP-AMS (FMI)
Pegasor Particle Sensor (PPS). Electrical charge of carried by particles.	Pegasor
Sample pre-treatment with catalytic strippers (CS), thermodenuder (TD)	Pegasor, TUT
PM and its composition incl. anions, metals and PAHs **In-depth analysis**, e.g. PAM, SMPS, CPC, ELPI+, TUT-HTDMA	VTT, TUT, FMI

Test set-up

- Nine different BC/EC instruments.
- A number of in-depth analyses.
- Complex dilution set-up for MAAP and aethalometers. Heated diluters.
- Sample pre-treatment (CS, TD).
- Gaseous emissions.
- Daily protocol and best practices followed.



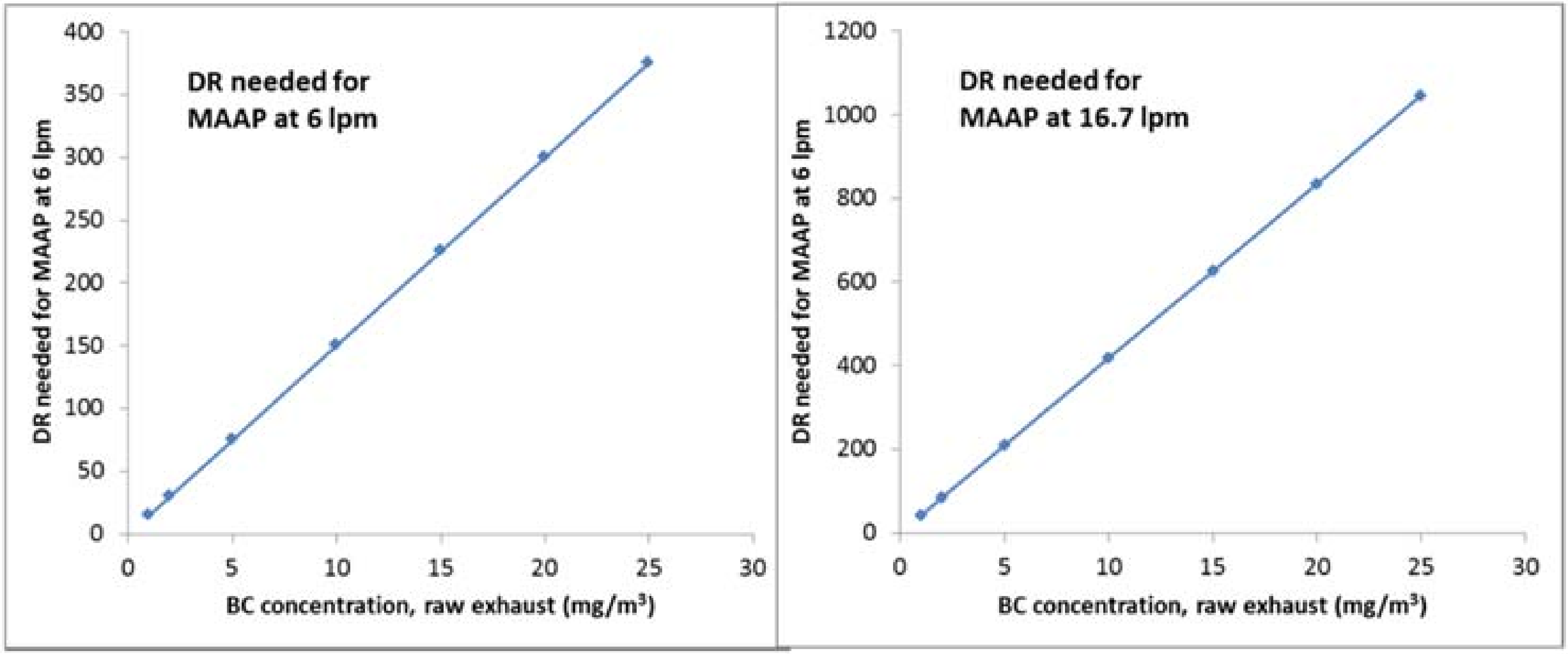
Challenging high dilution ratios (DR) needed for MAAP at high BC concentrations

Multi-stage dilution set-up is complex and extensive instrumentation, procedures and experienced personnel needed .

- CO_2 on-line at different locations, also from dilution air. CO_2 contamination risk.
- T, RH, impurities of dil air monitored. Ultra-pure dil air (wo CO_2) recommended.

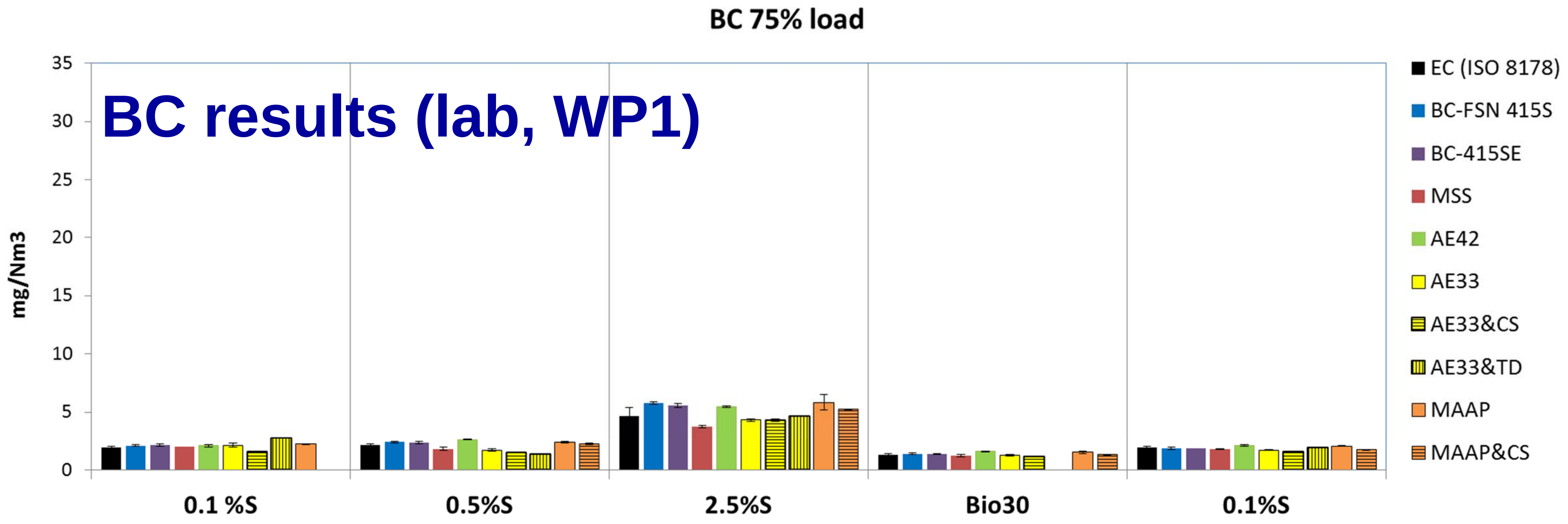
High DRs are **challenging in laboratory and not practical on board**.

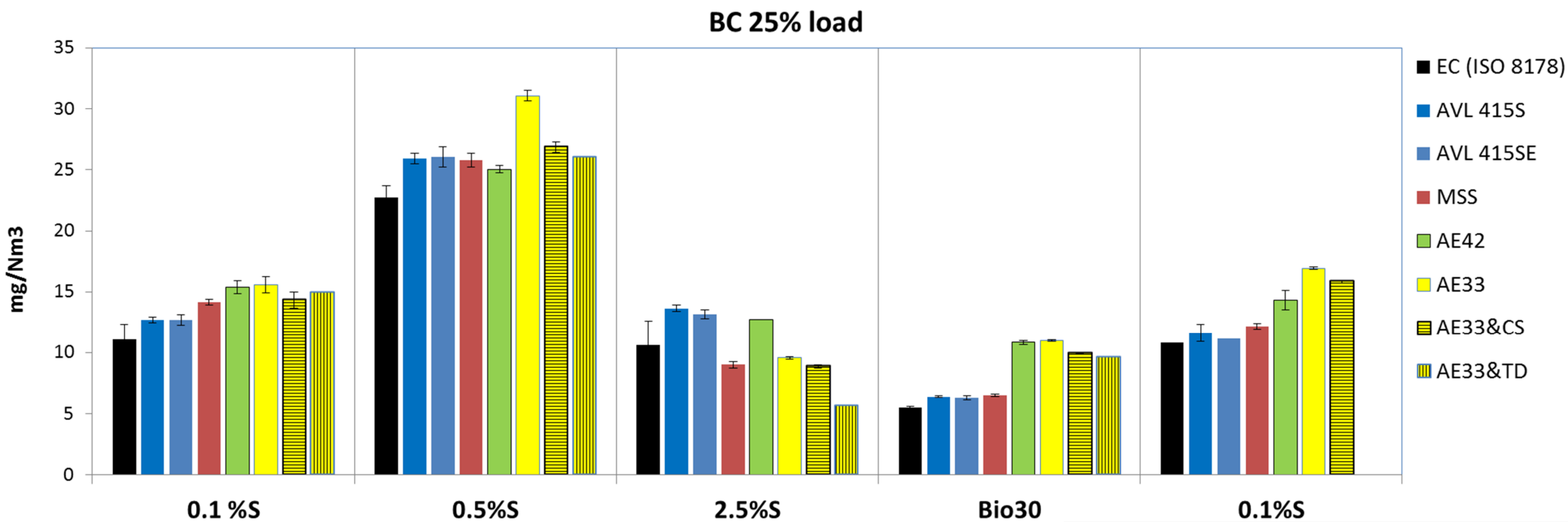
DR is a multiplier in the BC calculation → bias is directly reflected in BC. Dilution for MAAP needs to be sufficient to keep BC < 30 µg/m³.



	Pros	Cons
Raw exhaust measurements (BC based on FSN)	• No need for pressurised air and filteration or drying (typically) • Simple installation • No need to consider the uncertainty of dilution ratio	Condensation of sample gas to be avoided
Instrument's own dilution, low dilution ratio (AVL MSS, Pegasor PPS)	• Low risk of condensation of the sample gas • Simple system • Manufacturer's procedures for calibrations and quality assurance	• Pressurized air needed from ship (or small compressor) • Filteration and drying of the dilution air • More complex installation and more devices compared to a raw measurement • Increases uncertainties to some extent
High dilution ratios DR>>100 (MAAP, aethalometers)	Good for research purposes	• Not for regular ship BC measurements • Complicated test set-up • Experienced operators needed • High uncertainties due to DR

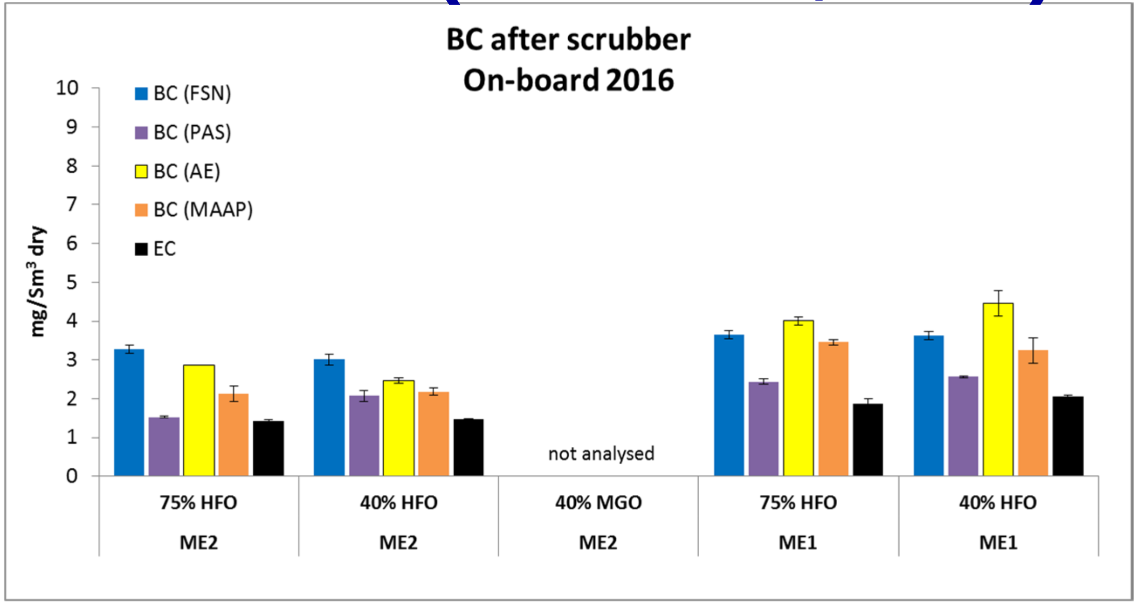
BC results (lab, WP1)

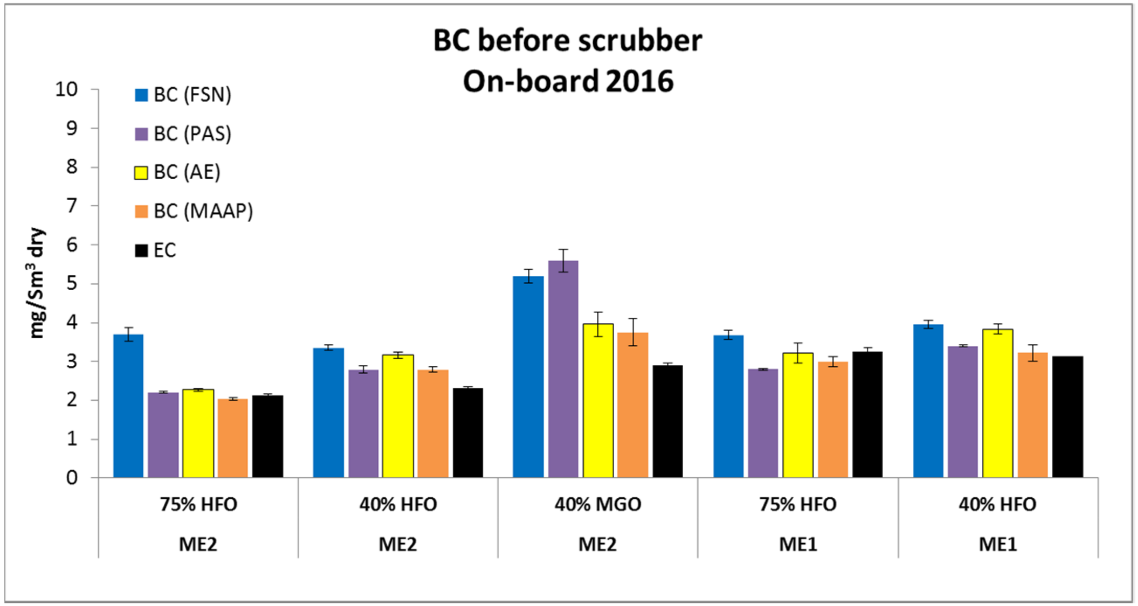




Ref. CIMAC Paper no. 068, 6-10 June 2016.

BC results (on-board, WP2)





In laboratory (WP1) and on-board (WP2), **comparable BC results were achieved with** 2xFSN, AVL MSS (PAS), MAAP and aethalometers. However measurements were demanding for some instruments.

All instruments rated fuels and loads in the same order regardless of their measuring principles.

CHALLENGES IN EC MEASUREMENTS

SEA-EFFECTS BC work on EC

Pre-studies:

- Three temperature programs:
  a) NIOSH 5040 with 870 °C peak T in He phase
  b) NIOSH 5040 with 750 °C peak T in He phase
  c) “EUSAAR2” with 650 °C peak T in He phase. → **Selected for tests.**
- Pre-treatment was studied, but not used for actual samples
  - Drying of filters (180 °C, 1 h)
  - Extractions of filters with a) toluene followed with IPA/water b) water only.
- Interpretation of thermograms

Round-robin in three labs:

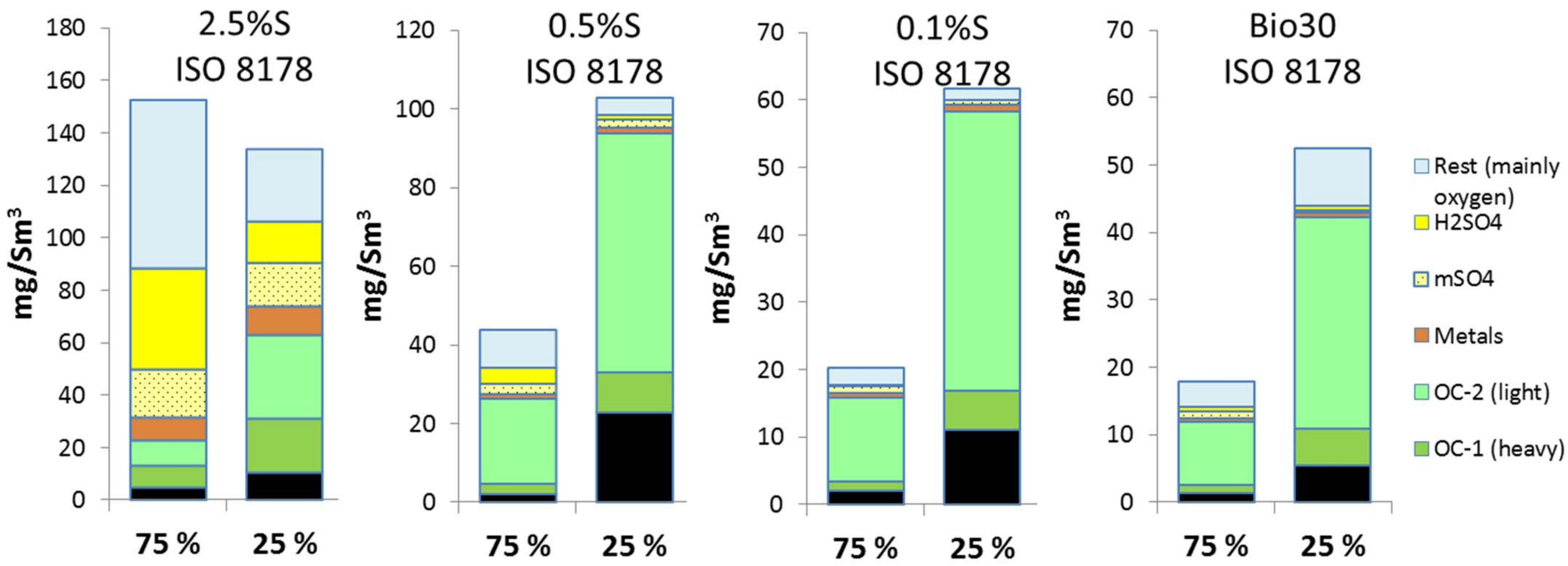
- 10 sample filters and one blank. Three punches from each filter for each laboratory.
- Sample treatment: no drying or extractions of loaded filters.
- EUSAAR2, last temperature step prolonged by 60 s
- Additional comparisons using a constant split of 750 s

Round-robin samples:

EC1 x 3	0.1 %S 75 %
EC2 x 3	0.1 %S 25 %
EC3 x 3	0.5 %S 25 %
EC4 x 3	0.5 %S 75 %
EC5 x 3	0.5 %S 25 %
EC6 x 3	2.5 %S 75 %
EC7 x 3	2.5 %S 25 %
EC8 x 3	Bio30 75 %
EC9 x 3	Bio30 25 %
EC10 x 3	0.1 %S 75 %
EC11 x 3	reference

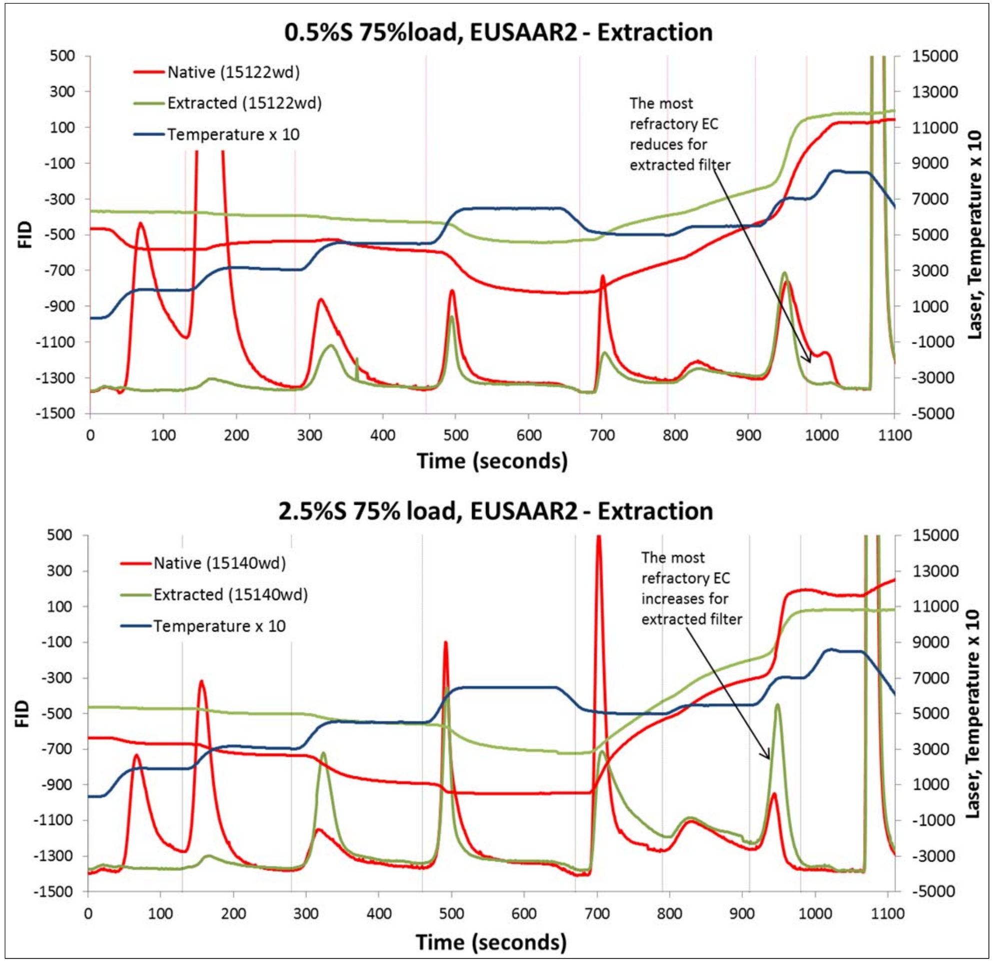
Composition of ship PM

Low share of EC in ship PM (high-speed on-road engines have a high EC share).



Extractions of filters

- Differences seen in the refractive EC
  - 0.5%S: EC lower after extraction. Possibly PM contains OC/PC tightly attached in EC.
  - 2.5%S: EC higher after extraction. Possibly premature EC combustion w/o extraction.
- Concerns with extractions
  - Risk for mechanical losses or movements of EC during extraction.
  - Changes in the most refractory EC deserve further studies.
  - OC cannot be determined after extraction.
  - Time-consuming.
- Positive: The automatic split could be used for all extracted samples.

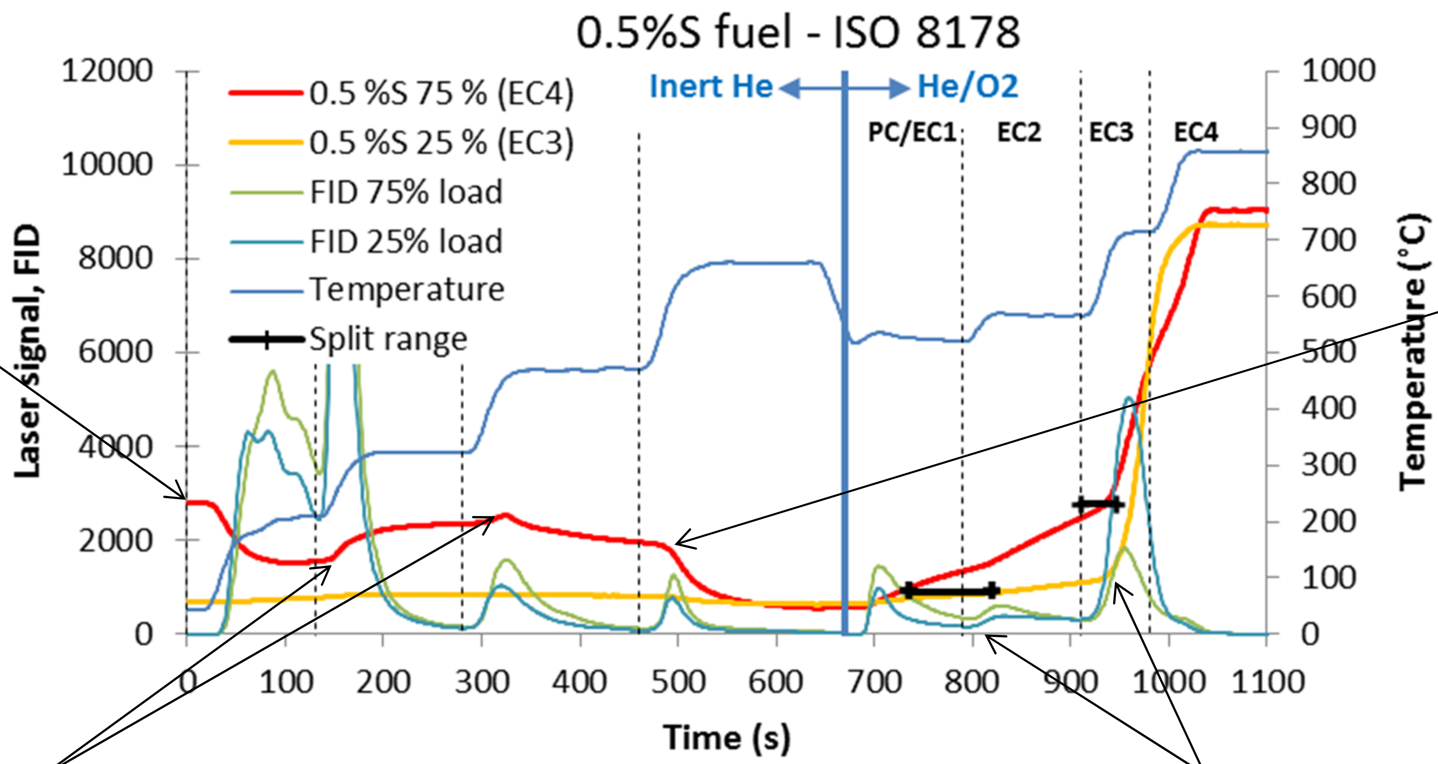


Example of challenging thermogram

(example 0.5%S, 75%, ISO 8178 PM)

Early drop in laser signal at <200 °C.

Automatically deemed as the start of pyrolysis, even if it was due to drying of filters (risk of under-estimated EC).



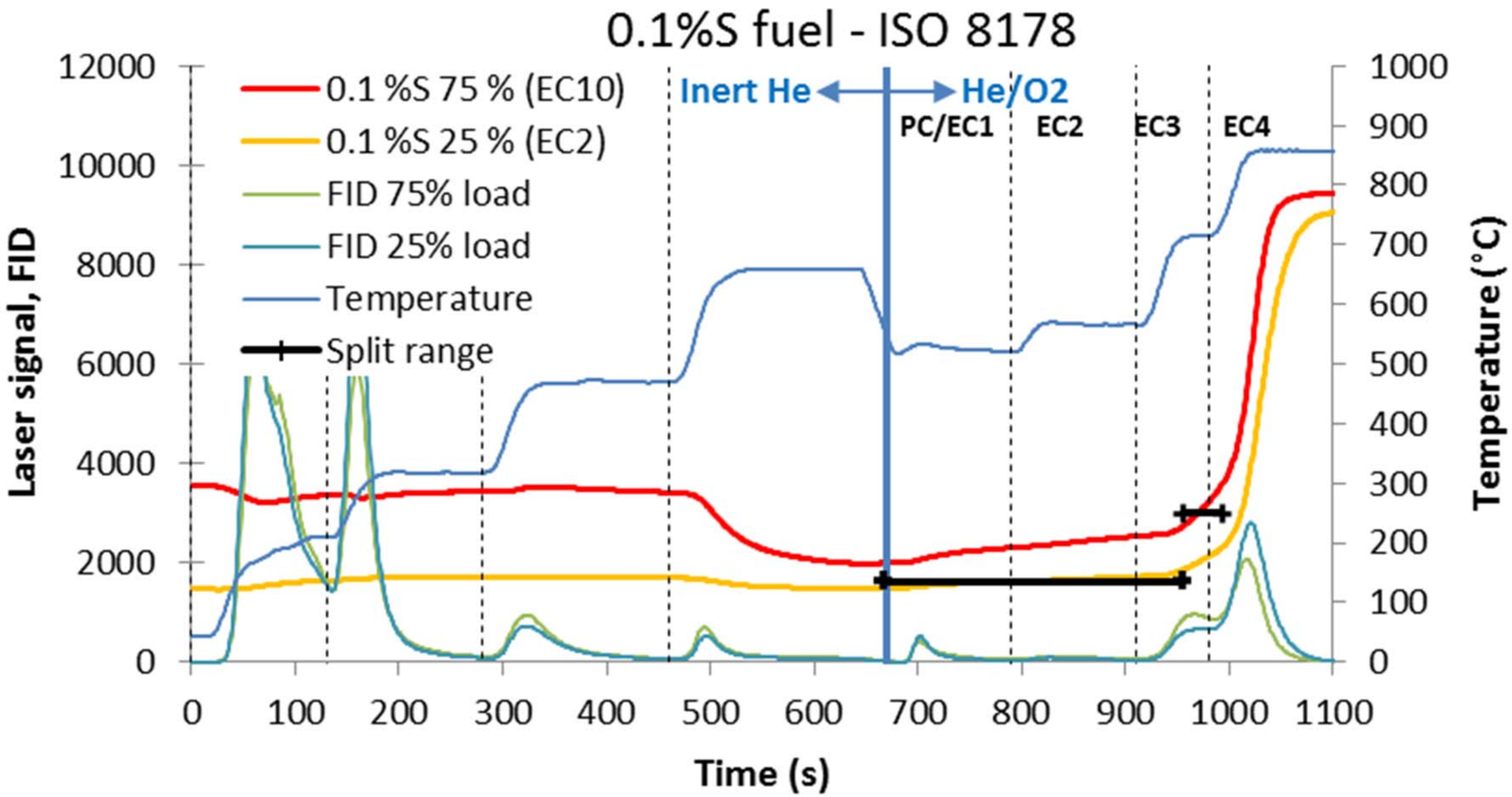
Pyrolysis starts (darkening). Asphaltenes are sources of char at 400-500 °C. (Barneto et al. 2014).

Increase in laser signal ~150 °C, ~ 350 °C. **Lightening of sample probably due to the evolving coloured OC**. Also other reactions e.g. evaporating crystal water could contribute.

When the split point is located in the region of substantial carbon output, small changes in the laser signals reflected in the split times may lead to substantial differences in the EC results, even if thermograms were similar in the EC part.

EC analysis for distillate fuels

For distillate fuels, EC combusted late. However, the spread of the automatically determined split time was high due to the early drop and small changes in laser signal.



Thermograms in the EC part were similar for all punches for one engine/load/fuel based on the constant split analysis → EC spread was due to the interpretations of thermograms.

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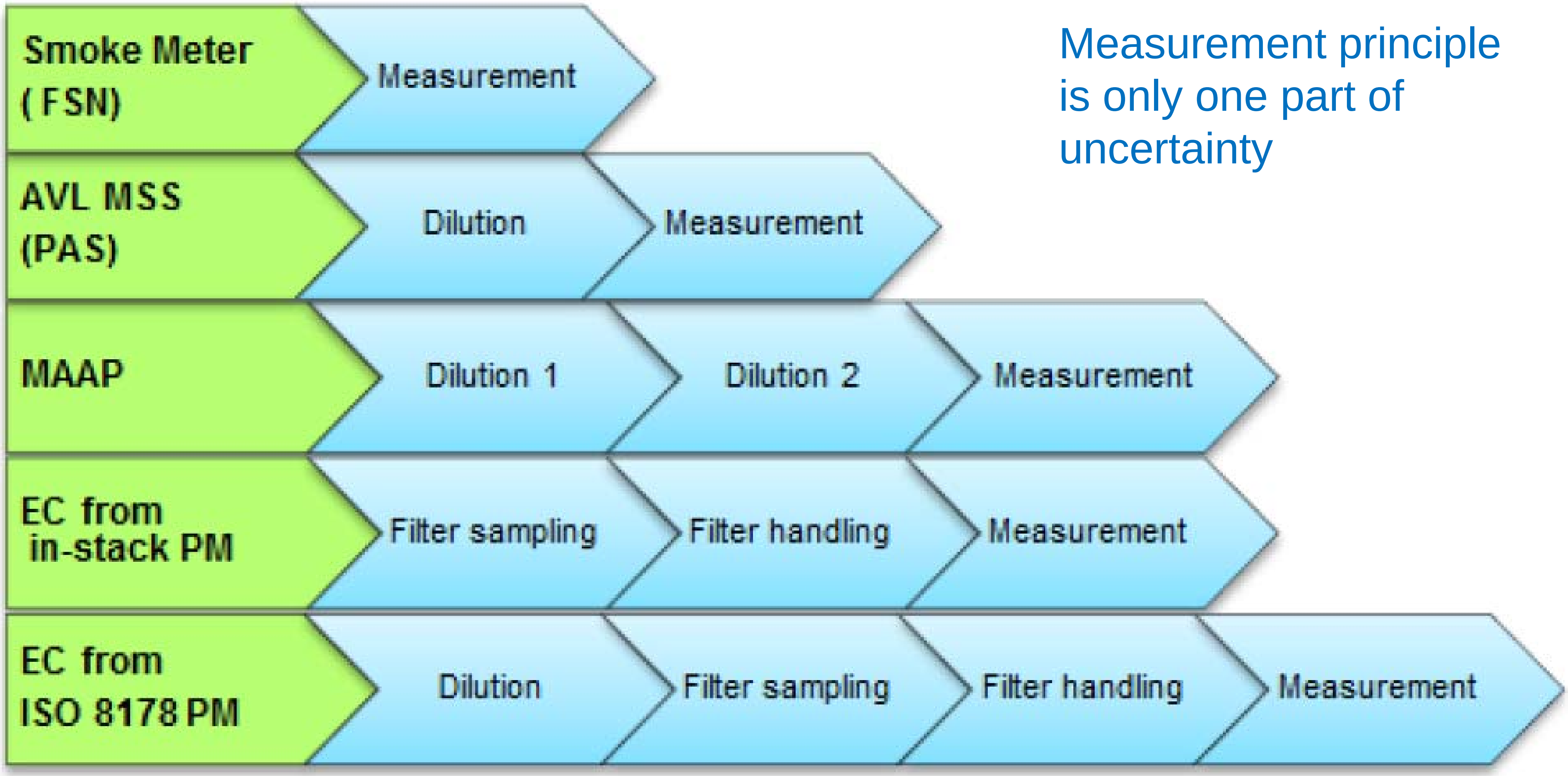
EC challenges

- **Ship PM is challenging** as it contains metals, OC (e.g. asphaltenes), sulphates, water.
- **Premature evolving EC** anticipated for samples having catalytic metals and/or oxygen.
- **Large amount of heavy OC** prone to pyrolysis may bias BC (despite of PC compensation).
- **Misinterpretation of thermograms** due to e.g. wet filters, multiple overlapping reactions, simultaneous transformations, colour changes → EC/OC split uncertain.
- Low/high filter loading, sample colour as well as instrumental issues e.g. drift of laser, optical correction principle are also of concern.

Extractions of filters could alleviate artefacts, but may induce new problems. Temperature program could be further developed for ship PM.

Pros	Cons
• Well-known and documented • Calibration procedures are available • Standardised procedures, such as NIOSH 5040 and proposal prEN 16909.	• Sensitive towards PM constituents. • PM sampling is required. • EC/OC split determination is uncertain. • Temperature program and standards mot designed for ship PM samples. • Restricted for use in laboratory. • No EC standard (saccharose for OC).

Building blocks of uncertainty



Measurement principle is only one part of uncertainty

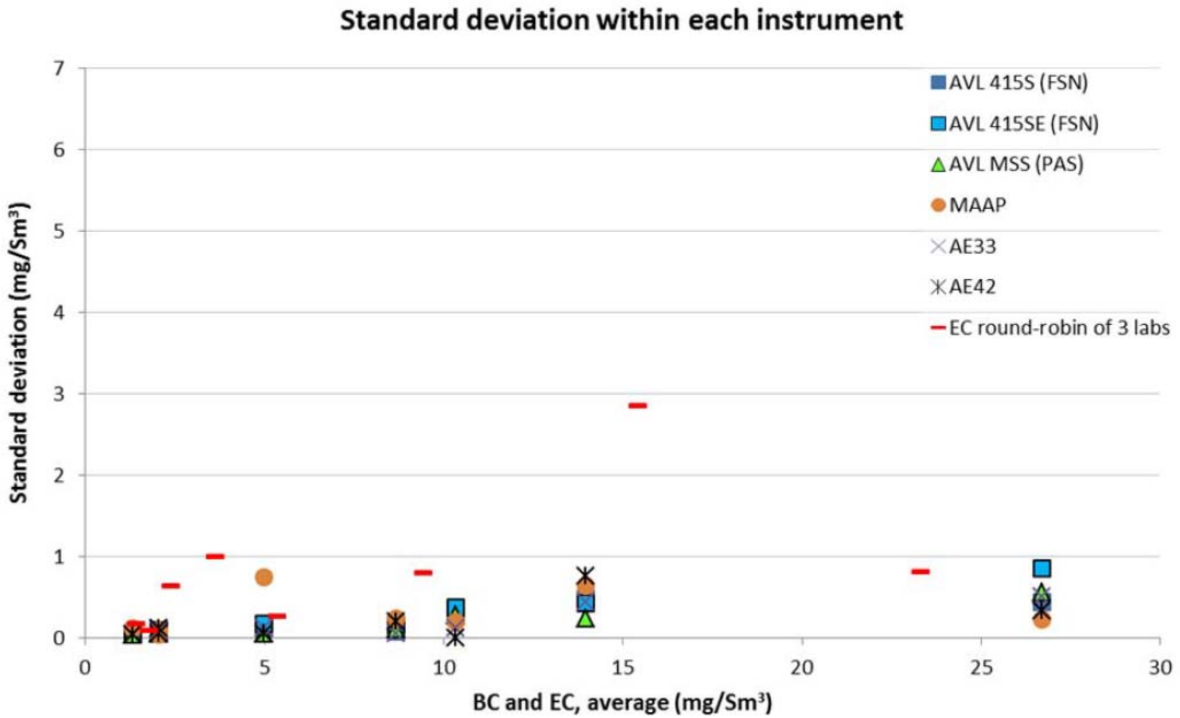
Standard deviation (SD), WP1 laboratory

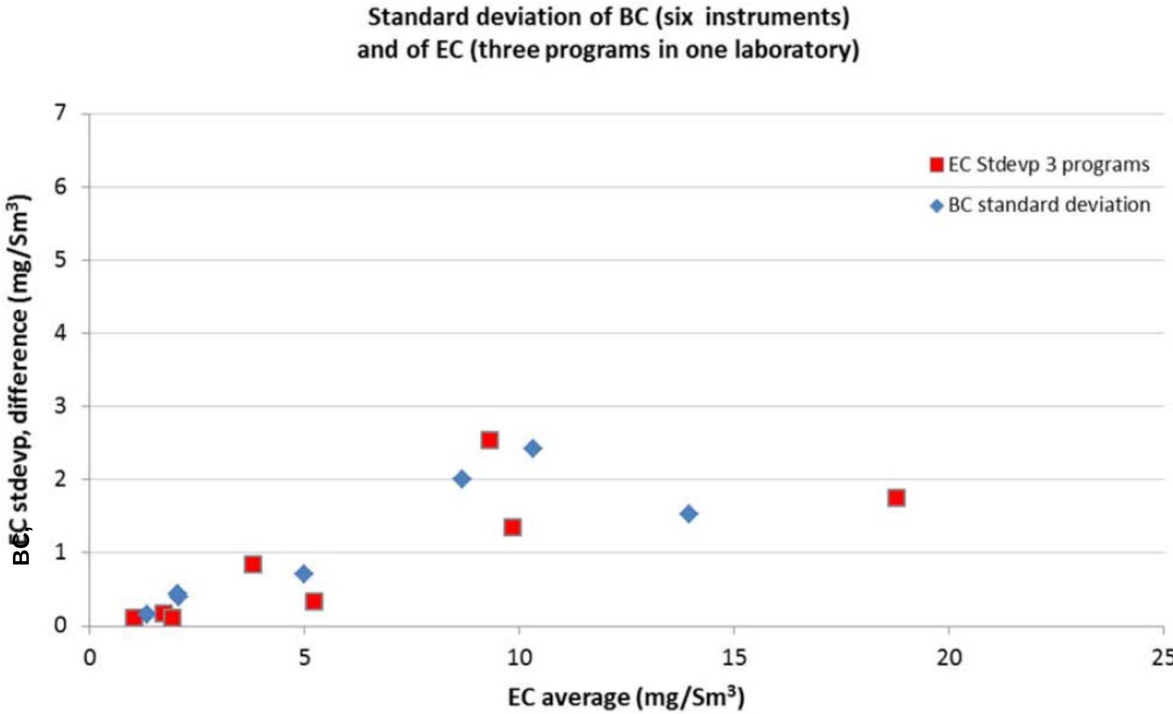
At BC level <10 mg/m³

- One BC method in one lab: BC SD <0.5 mg/m³ (<13 mg/kg fuel or <3 mg/kWh for engine studied).
- Different BC methods in one lab, BC SD <3 mg/m³.

At EC level <10 mg/m³

- One temperature program in 3 labs, EC SD <1 mg/m³.
- Three temperature programs in one lab, EC SD <3 mg/m³.





Summary

Instruments for BC measurements

- **Best performance with instruments designed for the exhaust measurements** (FSN, PAS), while challenges with those designed for ambient measurements (high DRs for e.g. MAAP).
- **Comparable BC results achieved with all instruments** when requirements were met.
- **Pretreatment (CS, TD)** may alleviate BC bias, but at the cost of increased complexity. **Heated diluters** for high-sulphur fuels needed (clogging/corrosion risks).

EC challenges

- Sensitive towards PM constituents.
- Potential misinterpretations of thermograms.
- Long chain from PM sampling to EC analysis in laboratory.
- EC procedure designed for ship PM is needed.

Not all IMO candidate methods are recommendable to be used in practise.

On-board a ship, heavy and large instruments are not desired.

Summary

- In the laboratory for an old engine, the results unveiled dependences between BC, fuel types and engine loads. **BC was not directly dependent**, while PM was dependent on the fuel sulphur content.

- On-board measurements on **a modern cruising ship showed low BC** from two different size engines at two loads and two different fuel types (HFO, MGO). No significant impact of scrubber (or SCR) on BC was observed.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