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Traceability of BC measurements

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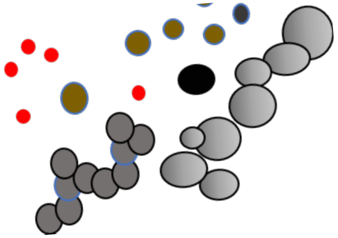
19.9.2019

Can BC measurement result be traceable?

- "Property of a measurement result whereby the result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty"

Issues related to traceability of BC measurements?

- **Issue 1**: BC is not a single compound and there are no "standard BC material"
- **Issue 2**: there are no "reference instruments" showing correct BC results
- **Issue 3**: there are instruments that measure black carbon that are based on very different techniques (optical, photoacoustic, thermal, incandescence, size distribution etc).
- **Issue 4**: different calibration factors/multipliers (e.g. MAC) are needed to calculate the result from measured quantity
- **Issue 5**: different units for BC are used in different sciences (Absorption Mm^{-1}, concentration $\mu g\ m^{-3}$, emission factors mg/km, mg/kwh, mg/kg fuel etc)



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Traceability to BC measurements is desperately needed

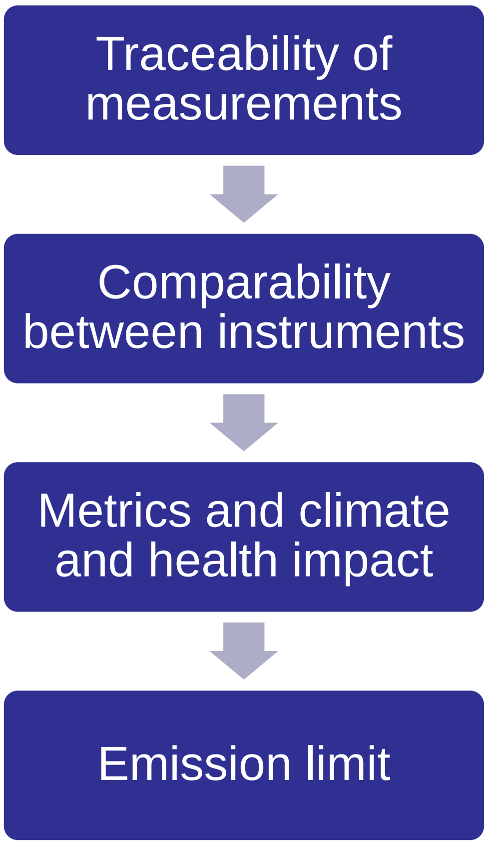
- Current large uncertainties in measuring BC -> comparing results from different instruments difficult
- Large amount of BC measurements conducted globally -> comparison between sites challenging, also trends hard to observed
- Emission limits for BC are currently considered by several different entities!
- Linking the BC result to health and climate impact challenging if there is large uncertainty in results
- Communication about BC related issues challenging. What is a large concentration of BC? How to explain it to people?

Ambient air and ship exhaust are different – challenge for instruments!

	Ambient	Ship exhaust 0.5%S fuel [a]
BC concentration, µg/m^3	1-20	1000-15 000
Temperature, °C	-30- +30	>200
Water vapour, %	0-100	~10
NO_x, µg/m^3	<500	2 000 000
SO_2 µg/m^3	<50	300 000
PM µg/m^3	<1000	45 000
PM-H_2SO_4 µg/m^3	<20	4 000
PM metals, e.g. V, Ni, Ca, µg/m^3	<10	1 000

* SEA-EFFECTS BC project (Aakko-Saksa et al. Research report VTT-R-02075-17, WP1)

Chain from measurements to impact needs to be known to set meaningful emission limits



EMPIR BC – developing reference material + traceable methods (2017-2020)

SEAEFFECT BC – intercomparison of BC instruments on ship emissions (2015-2017)

BC Footprint – to improve understanding on bc related issues and to develop a metrics for BC (2019-2022)

EMPIR BC

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The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

EMPIR BLACK CARBON

16ENV02 Black Carbon project

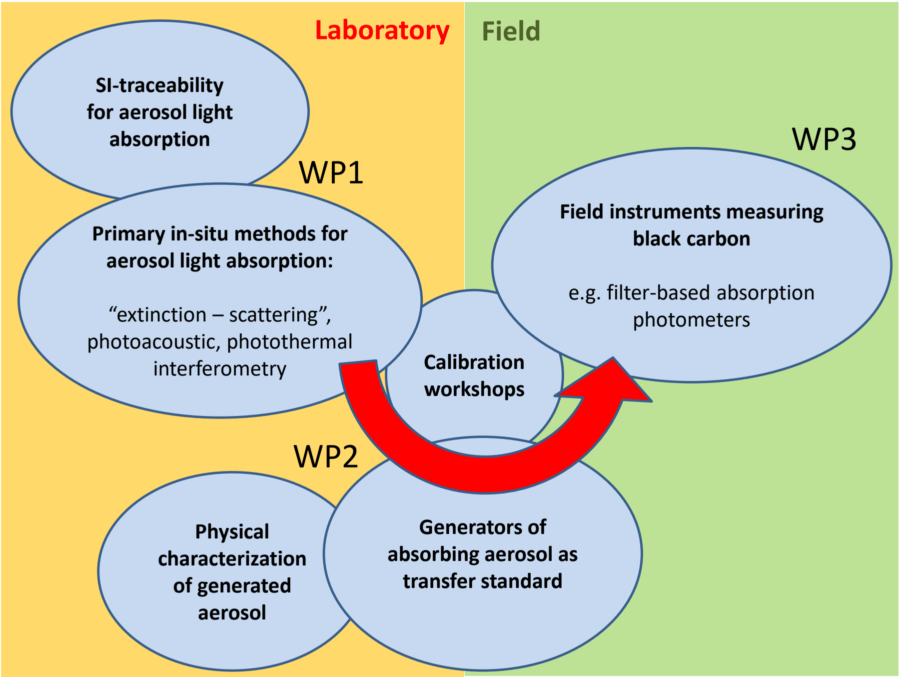
July 2017 – June 2020

Project coordinator: Paul Quincey, NPL/UK

..is kindly acknowledged for the slides

Other project partners:
TROPOS (Germany)
PTB (Germany)
NCSR Demokritos (Greece)
METAS (Switzerland)
FHNW (Switzerland)
PSI (Switzerland)
LNE (France)
FMI (Finland)

..are kindly acknowledged for the project results



Project objectives

1. To establish **a set of well-defined physical parameters, such as aerosol light absorption coefficients and mass absorption coefficients**, which together can be used to quantify black carbon mass concentrations with traceability to primary standards. (WP1)

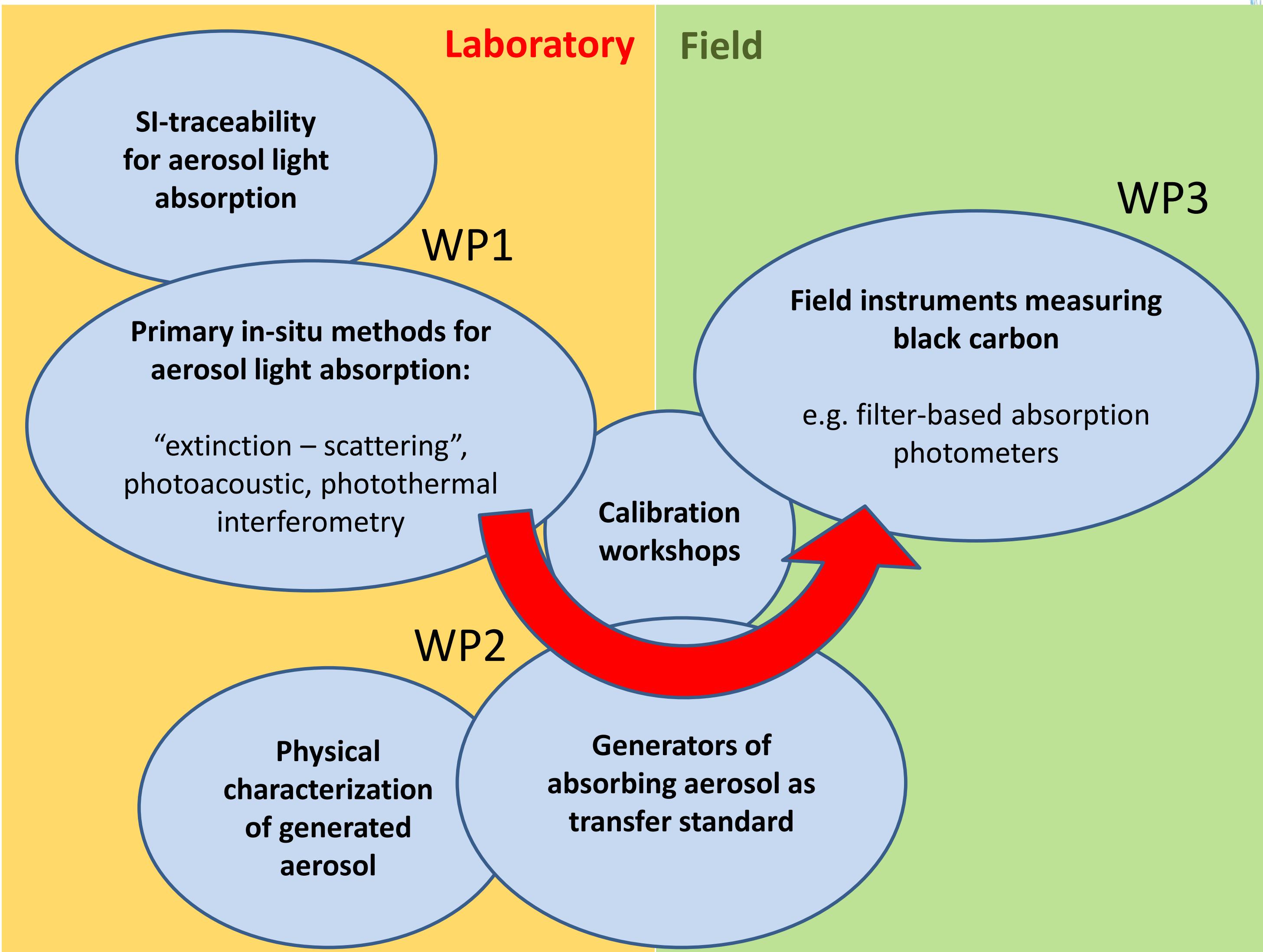
2. To develop and characterise black carbon **standard reference materials (SRMs), representative of atmospheric aerosols**, together with methods for using them to calibrate field black carbon monitors. (WP2)

3. To develop a **traceable, primary method for determining aerosol absorption coefficients at specific wavelengths** that are to be defined for the benefit of users. The method should have defined uncertainties and a quantified lowest detection limit. (WP1)

4. To develop a **validated transfer standard** for the traceable calibration of established absorption photometers such as multi angle absorption photometers, aethalometers and particle absorption photometers. The transfer standard should make use of the black carbon SRMs (developed in objective 2) and associated portable instrumentation characterised by the primary method (from objective 3; in WP3).

5. To facilitate the take-up of the technology and measurement infrastructure developed in the project by standards developing organisations (CEN, ISO) and end users (e.g. Environmental Protection Agency (EPA), European Environment Agency (EEA), World Meteorological Organisation-Global Atmosphere Watch (WMO-GAW), the ACTRIS (Aerosols, Clouds, and Trace gases Research InfraStructure Network) Project). (WP4)

Overview: metrology for light absorption by atmospheric aerosols



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Choise of SRM generator methods results of intensive laboratory testing

16ENV02 EMPIR Black Carbon - Deliverable D4

Recommendations for black carbon standard reference materials (SRMs) and ancillary equipment suitable for calibrating field black carbon monitors

<u>Potential generators</u>

Diffusion flame mini-CAST

Pre-mixed flame mini-CAST

Miniature inverted soot generator

Nebulisation
- **Aquadag® (colloidal graphite)**
- **Fullerene soot**
- **Black-dyed PSL**

Spark discharge generators

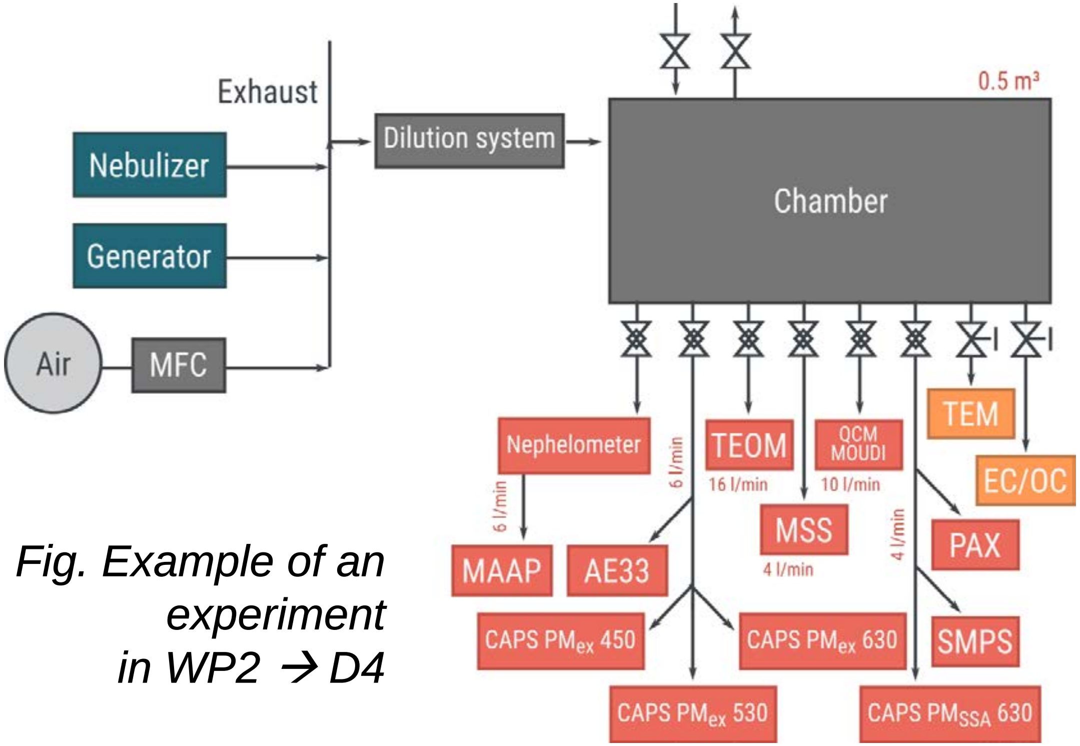


Fig. Example of an experiment in WP2 → D4

Project achievements

1 Establishment of calibration rationale:

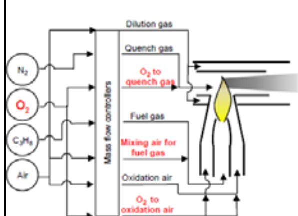
Calibration with one aerosol type is not viable. Two contrasting types of calibration aerosol were agreed:

(1) "fresh combustion particles":
size 50 - 100 nm, SSA 0.05 – 0.2 at 550 nm

(2) "aged combustion particles":
size 200 - 400 nm, SSA 0.7 – 0.9 at 550 nm

3 Development of required aerosol sources

miniCAST 5201 BC



$C/O = n↓c / n↓O$

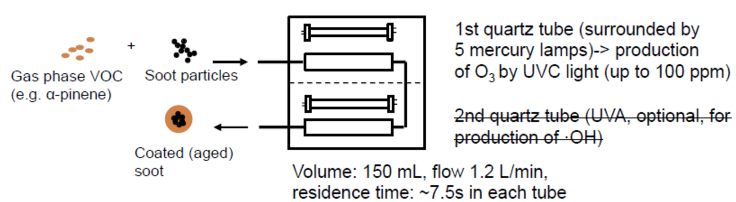
- Premixed and diffusion flame modes available

(new operation variables marked in red)

"fresh": miniCAST

"aged" : + micro smog

Micro smog chamber[1]



4 Field campaigns: clean & polluted

(1) Pallas station Finland: June – July 2019

(2) Athens, Greece: November 2019 – January 2020

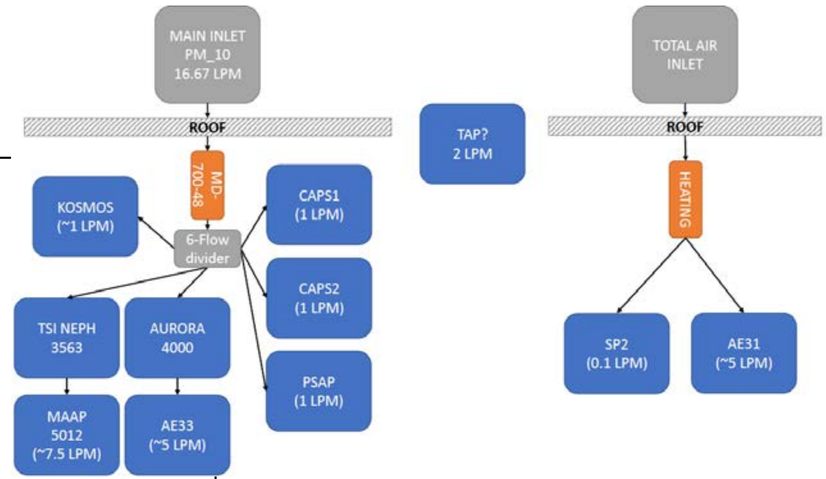


Fig. Pallas campaign instrument setup

Project achievements (2)

2 Improvements to traceable (filter-free) methods

Extinction minus scattering techniques

Critical issues

- Truncation correction of scattering measurement must be accurate & consistent
- Cross-calibration of scattering against extinction must be accurate & consistent (now about 2%)

TROPOS is investigating combination of $CAPS_{pmex}$ and Aurora4000 polar nephelometer

- New method proposed better correcting truncation error for absorbing particles. Method can be applied to polar Nephelometer Aurora4000
- Simple method for improving baseline correction of CAPS caused by NO_2

PSI is characterizing $CAPS_{ssa}$

- Characterization of the $CAPS_{ssa}$ truncation will lead to new truncation correction
- Measurements with monodisperse non-absorbing particles of the truncation correction available.
  - Reconciliation with model to be investigated
  - Investigate size and material dependency

Photothermal Interferometry

FHNW has improved the BC detection limit with time

Comparison of 4 “traceable” absorption measurement techniques

Instrument	EMS (extinction minus scattering)	PAX (photoacoustic extinctiometer)	CAPS$_{ssa}$	PTI (under development)
Principle	Extinction and scattering measured in separate instruments	Photoacoustic photometer and inverse nephelometry	Extinction and scattering measured in single cell	Photothermal effect
primary measurands	extinction coeff., scattering coeff.	absorption coefficient and scattering coefficient	extinction coeff. and scattering coeff.	absorption coefficient
calibration	calibration with certified Rayleigh scattering gas; cross calibration between instruments with non-absorbing aerosol	calibration with aerosols (calibration bound to internal extinction cell); systematic investigation of calibration with different aerosols missing	extinction needs to be calibrated, cross calibration between scattering and extinction	with certified absorbing gas
portability	high transportation effort, requires full calibration after transportation	good	good	to be tested
full traceability	yes	no	no, calibration with certified gases to our knowledge not reliable	under investigation
derived measurands	absorption coeff. Ångström exponent for multi wavelength	single scattering albedo	absorption coeff. and single scattering albedo	-
single/multi-wavelength	single or multiwavelength	three wavelength instrument available	single	single
applicability in field as absorption reference for ambient aerosols	high detection limit requires very high aerosol concentrations	detection limit sufficient	high detection limit requires high aerosol concentrations	detection limit at medium/ high concentration sufficient (to be tested)
applicability as primary or secondary reference for generated soot	primary standard in laboratory	secondary standard in laboratory and field	secondary standard in laboratory and filed	primary or secondary standard (traceability under investigation)

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Conclusions EMPIR BC

1. Standard Reference Material (SRM) must meet the specific purpose. It is different for fresh and aged atmospheric aerosol. Dependence on BC source.

2. The choice of traceable method for atmospheric aerosol absorption (or “equivalent Black Carbon”) thus far is the EMS (extinction minus scattering) –technique. Development ongoing also with other techniques.

3. Traceability to real atmospheric Black Carbon mass is a tricky problem. MAC highly variable.

4. Field calibration methods are under development. No recommendation yet.

SEA-EFFECTS BC

SEA-EFFECTS BC project, Finland, 2015-2016

Research organisations, authors

- 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, M. Bloss, S. Saarikoski, R. Hillamo
- Tampere University of Technology,TUT P. Karjalainen, N. Kuittinen, P. Simonen, T. Rönkkö, J. Keskinen
- University of Turku, 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, Oiltanking Finland 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), Neste, Metropolia, UEF, Gasera Oy

Acknowledge for financial support from Tekes (40356/14), Trafi (172834/2016) and industrial partners Wärtsilä, Pegasor, Spectral Engines, Gasmet, VG-Shipping, HaminaKotka Satama Oy, Oiltanking Finland Oy and Kine Robotics.

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

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Ambient and exhaust BC measurements

	Exhaust emission measurements	Ambient measurements	Stan-dard	Range etc.
Filter Smoke Number (FSN) **Designed for EXHAUST**	Raw exhaust	-	**YES**	AVL 415SE: 20ug/m3-32 000 mg/m³ Resolution: 0.01 mg/m³ DL: 0.02 mg/m³
AVL MSS (PAS) **Designed for EXHAUST**	Own diluter DR 2-20, 3.8 lpm	-	No	1ug-1000 mg/m³ (Range with dilution); Time basis up to 10 Hz, Rise time <1s, Sensitivity 5 µg/m³
TOA "EC/OC" **Designed for AMBIENT**	**Challenging sampling of** proper "lightness/darkness" filters at high EC conc. **Sample transportation** to post-analysis: contamination risk **PM metals/asphalthenes** → bias.	Sampling straightforward **PM metals / heavy compounds** near to wood combustion sources. **Sample transportation**: contamination risk	**YES**	EC range: 1-15 µgC/cm² DL: 0.2 µgC/cm² Repeatability ± 5%
Aethalometer AE33 **7 wavelengths. 880 nm BC.** **Designed for AMBIENT**	**High DR needed** for diesel (e.g. DR>600) → uncertainty **PM metals / asphaltenes** → bias	Straightforward **PM metals / heavy compounds** near to wood combustion sources.	No	Range: <0.01 to >100 µg/m³ Resolution: 1 ng/ m³, Sensitivity: ~0.03 µg/m³ DL (1 h): <0.005 µg/m³
MAAP **Designed for AMBIENT**	**High DR** needed for diesel (e.g. DR>600) → uncertainty	6 lpm (spec 16.7 lpm)	No	0-60, 0-180, µg/m³ BC @ 30, 10, average, DL: 2min. av <100 ng/m³; 10min. av <50 ng/m³; 30min. av <100 ng/m³; PM1 cyclone
SP-AMS **Designed for RESEARCH PURPOSES (AMBIENT)**	**High DR** needed for diesel (e.g. DR>600) → uncertainty	0.1 lpm (spec 1.5 lpm)	No	BC 0.04 µg/m³ -2 mg/m³ Time basis 1 min DL (1min): <0.04 µg/ m³ Measured size limited: 30 nm to 800 nm

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Sampling of raw or diluted exhaust

	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

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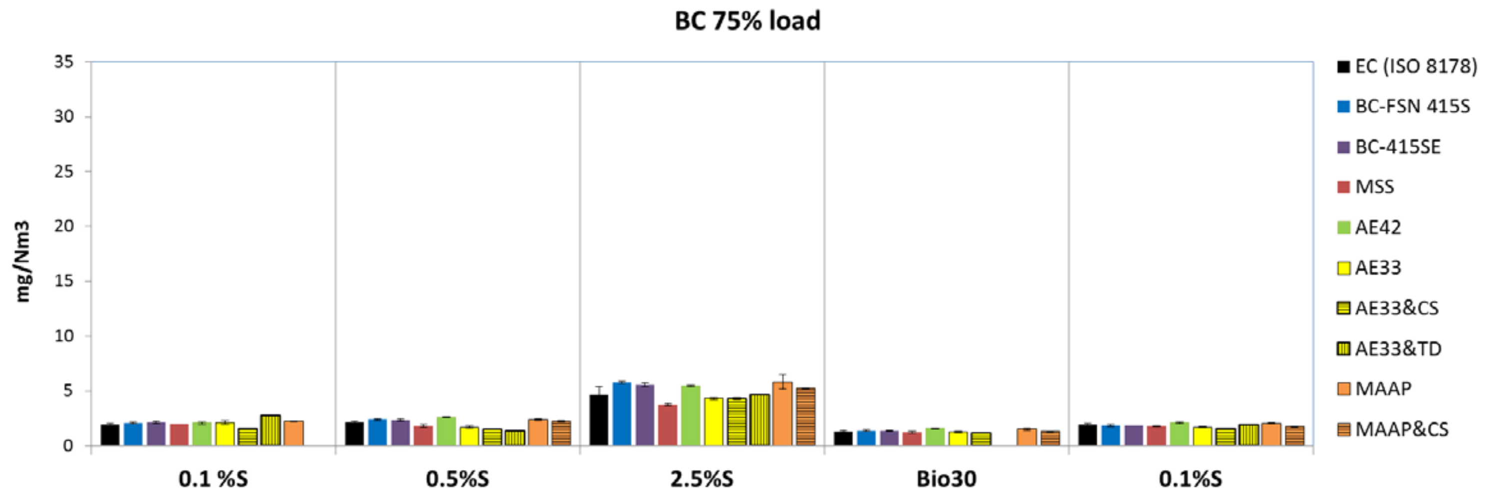
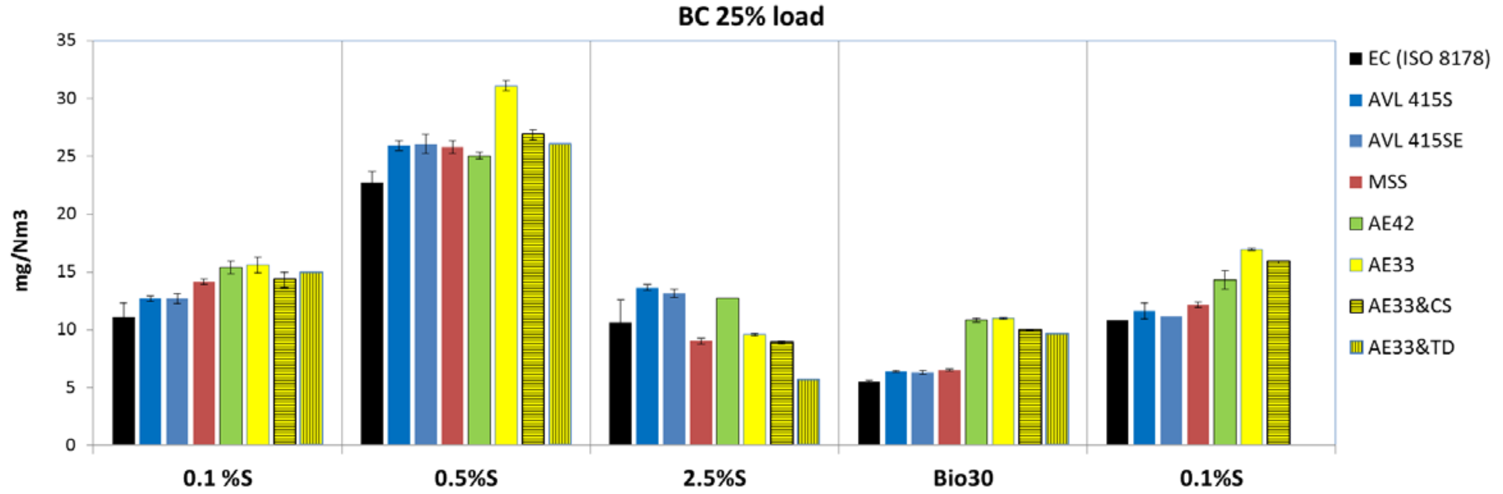
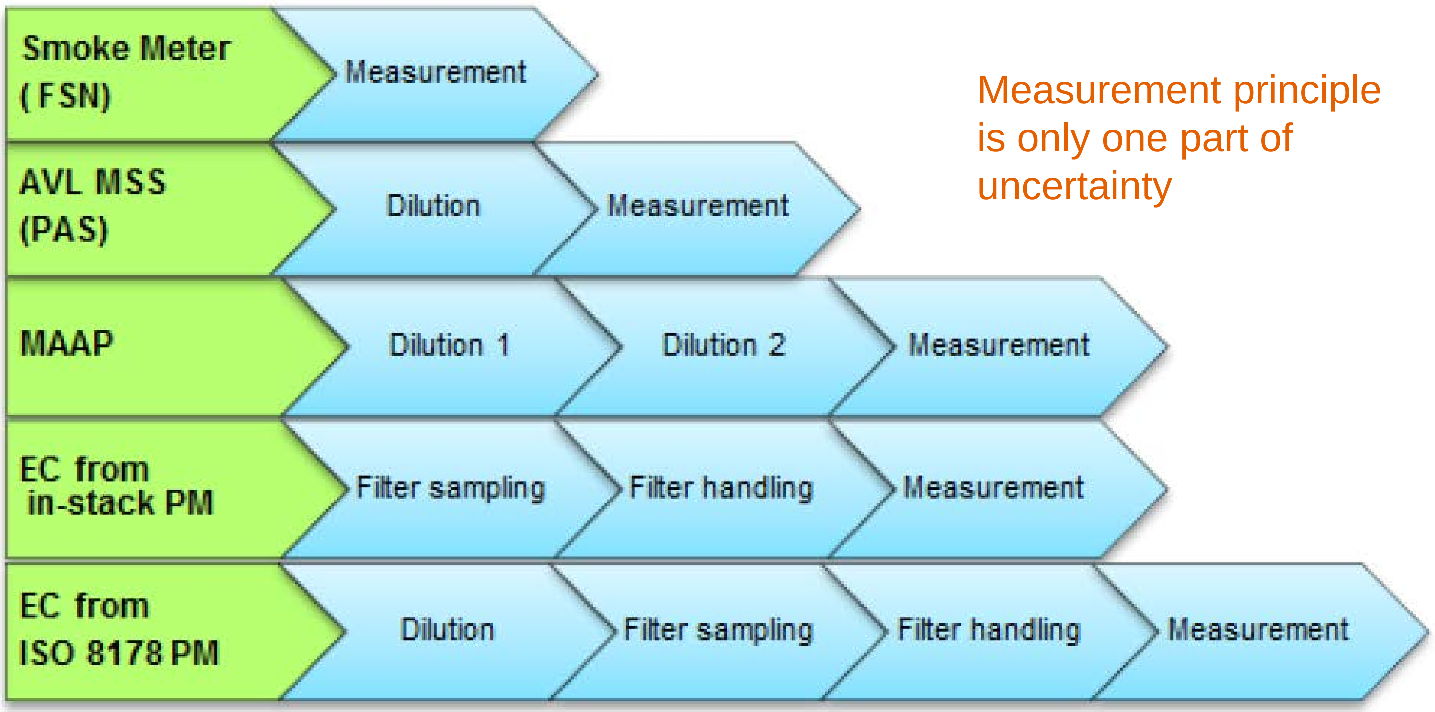
BC results (lab, WP1)





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

Building blocks of uncertainty



Measurement principle is only one part of uncertainty

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Findings on the BC emission instruments

- **Good performance with instruments designed for the exhaust measurements** (FSN, PAS). Instruments designed for ambient measurements need high DRs at high BC concentrations.
- **Comparable BC results achieved with all studied instruments** when requirements were met.
- **Pretreatment (CS, TD)** may alleviate BC bias, but at the cost of set-up complexity.
- **Heated diluters** needed for high-sulphur fuels (clogging/corrosion risks).
- **EC challenges:** Ship PM constituents may lead to misinterpretation of thermograms. Long chain from sampling to lab analysis. (EC/OC article 2018)
- **On-board a ship, heavy and large instruments are not desired**.

Examples on other findings:

- **Old engine (lab): Higher BC at 25% than at 75% engine load. At 75% load, higher BC for the 2.5%S HFO fuel** than for other fuels studied**. At 25% load, high BC for the 0.5%S fuel**. Lowt BC for the Bio30 fuel.
- **On-board, two modern ships: Low BC at 75% and 40% engine loads for HFO and MGO**.

BC Footprint

BUSINESS FINLAND

Black Carbon Footprint

Topi Rönkkö, Tampere University

Hilkka Timonen, Finnish Meteorological Institute

Research partners:

SYKE

VTT

UNIVERSITY OF EASTERN FINLAND

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BC Footprint project

- 3 year project (2019-2022)
- Funded by Business Finland
- Consortium consists of
  - 5 research institutes (TAU, FMI, VTT, UEF, SYKE)
  - 8 companies
  - 2 cities
- Main aim: This project will develop a Black Carbon Footprint concept that can be used as a uniform metrics for the BC, covering the whole chain from BC emissions to atmospheric BC concentrations and climatic effects.

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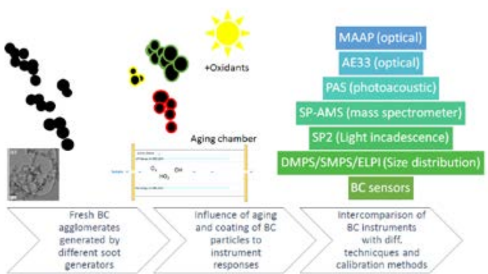
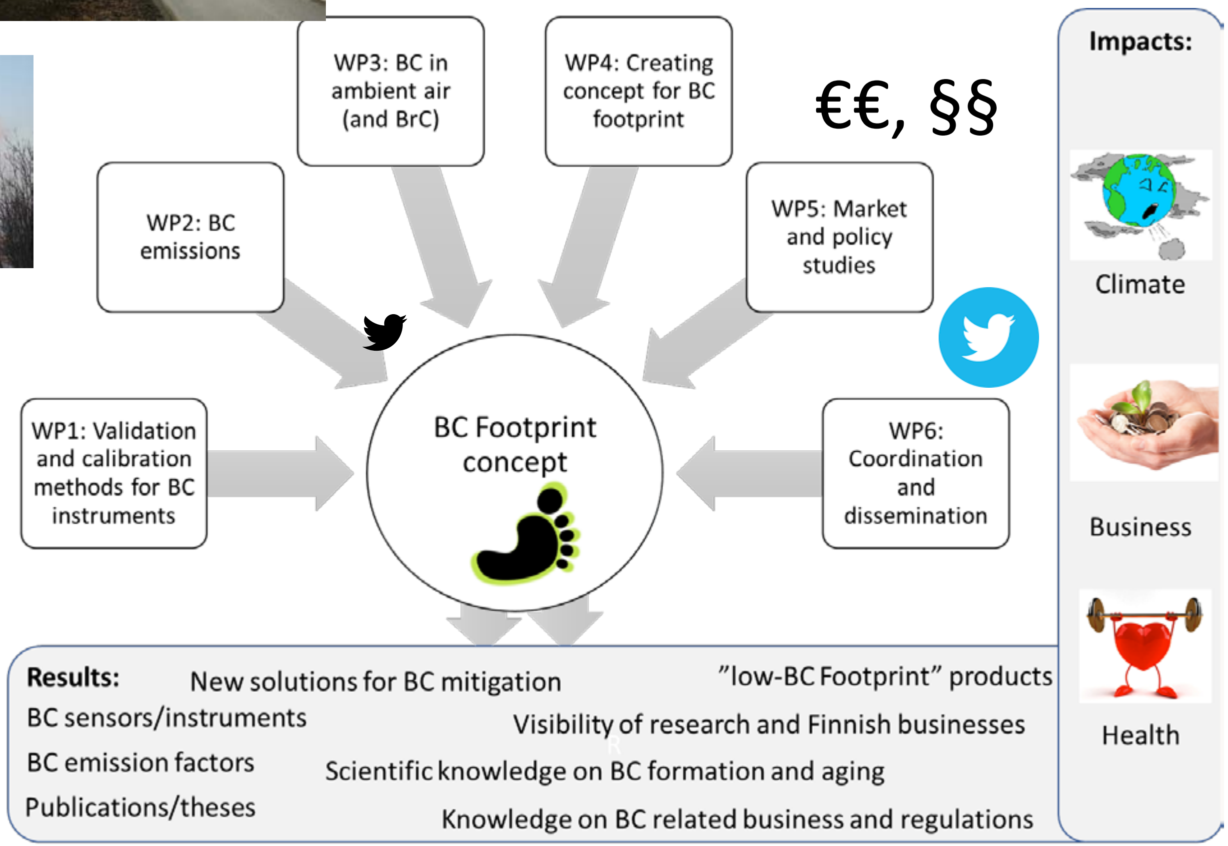
WP structure of BC Footprint





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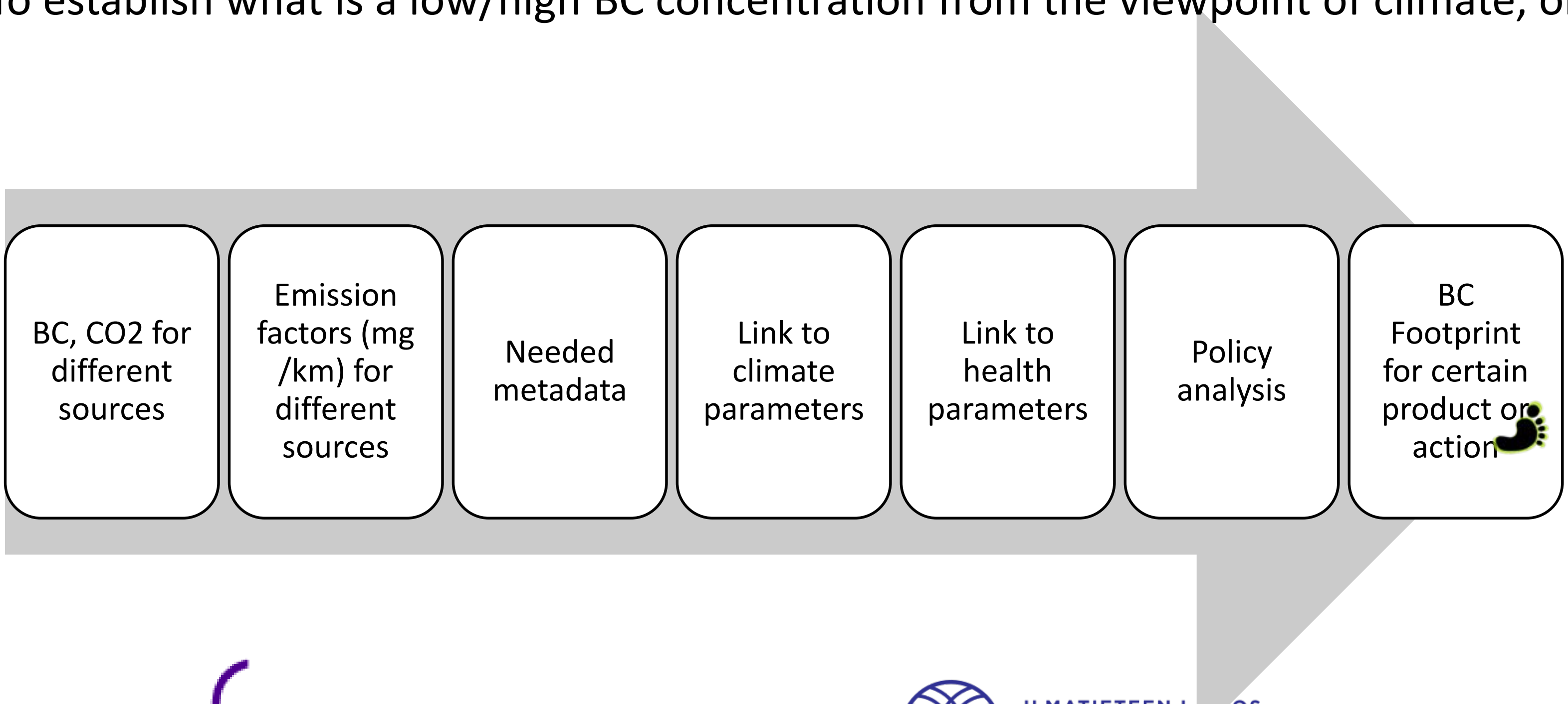
BC footprint concept

- Based in best cientific knowledge and BC emission factors for different sources
- Analogy to CO_2 footprint
- Use examples:
  - climate impact of biofuel combusion
  - influence of aftertreatment systems
- To establish what is a low/high BC concentration from the viewpoint of climate, or health



BC Footprint project

- Started 07/2019
- Twitter: @BCFootprint
- Internet: www.bcfootprint.com
- Interested to hear more?
  - Contact: Topi Rönkkö (topi.ronkko@tuni.fi) or Hilkka Timonen (hilkka.timonen@fmi.fi)

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Conclusions

- Althought BC measurements have been conducted over 30 years, there are still a lot of issues
- BC measurements are not currently traceable
- Comparability of different methods depend on the sample matrix
- Methods are often developed either to ambient or emission measurements, and may not be optimal for the other purpose (wrong calibration range, timeresolution, flow etc..)
- To set limits, it would be important to understand the link between BC and climate/health/air quality better!
- **To create regulations (emission limits, laws etc), BOTH traceable BC measurement methods and established metrics for BC are needed!**

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Thanks

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