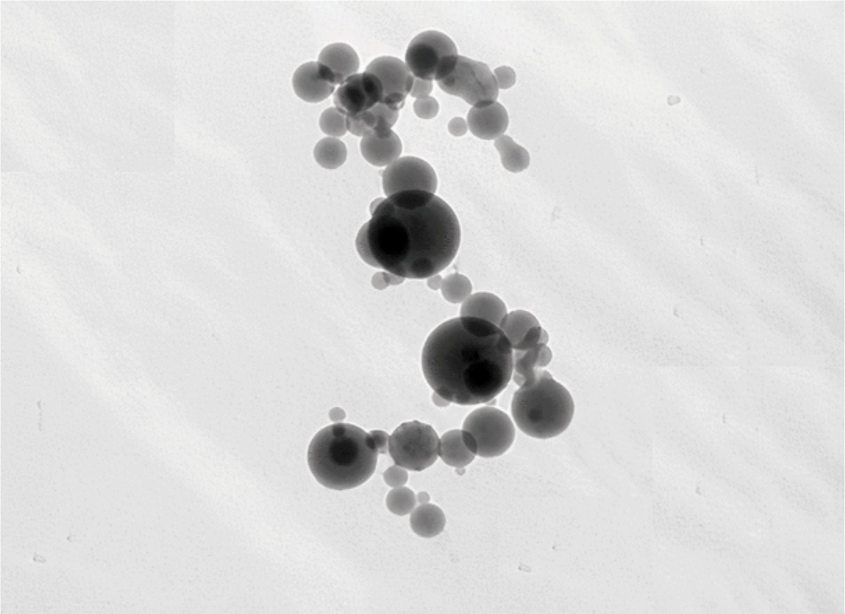
Optical properties of coated black carbon aggregates with changing size, morphology, and composition



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Optical properties of coated black carbon aggregates with changing size, morphology, and composition

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Second Ph.D. Talk
22/10/2020

Ph.D. Committee : Prof. Dr. Alfred Wiedensohler, Prof. Dr. Johannes Quaas, and Prof. Dr. Harmut Herrmann.

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Optical properties of coated black carbon aggregates with changing size, morphology, and composition

Contents

- ❖ Background
- ❖ Modelling and parametrization
- ❖ Experimental validation
- ❖ Summary
- ❖ Outlook

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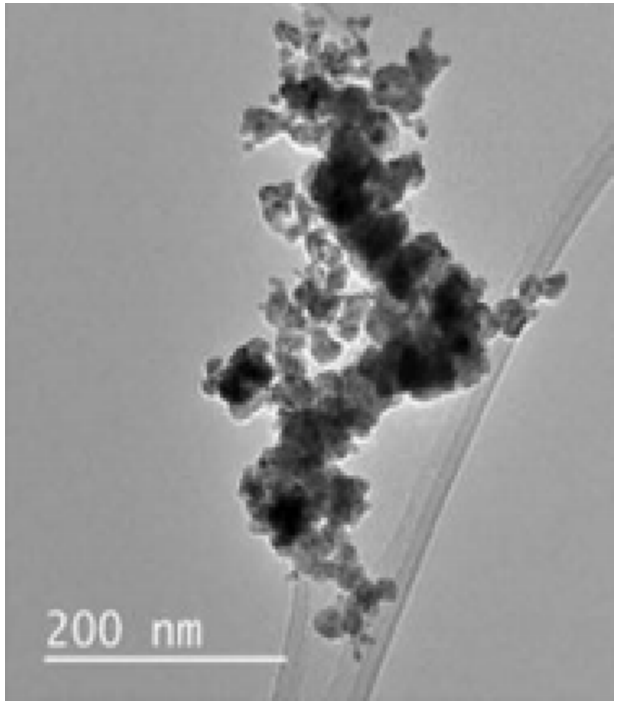
Black Carbon?

- Black Carbon (BC) belongs to the **fine particulate matter.**

- These particles **strongly absorb** solar radition.



Lie et al., 2008.

SOURCES

Traffic

Cooking

Power Plants/ Industries

Bio-mass burning

Google.

At microscopic level…

- BC particles consist of agglomerates made up of numerous primary particles

↓

Black Carbon Fractal Aggregates (BCFAs)

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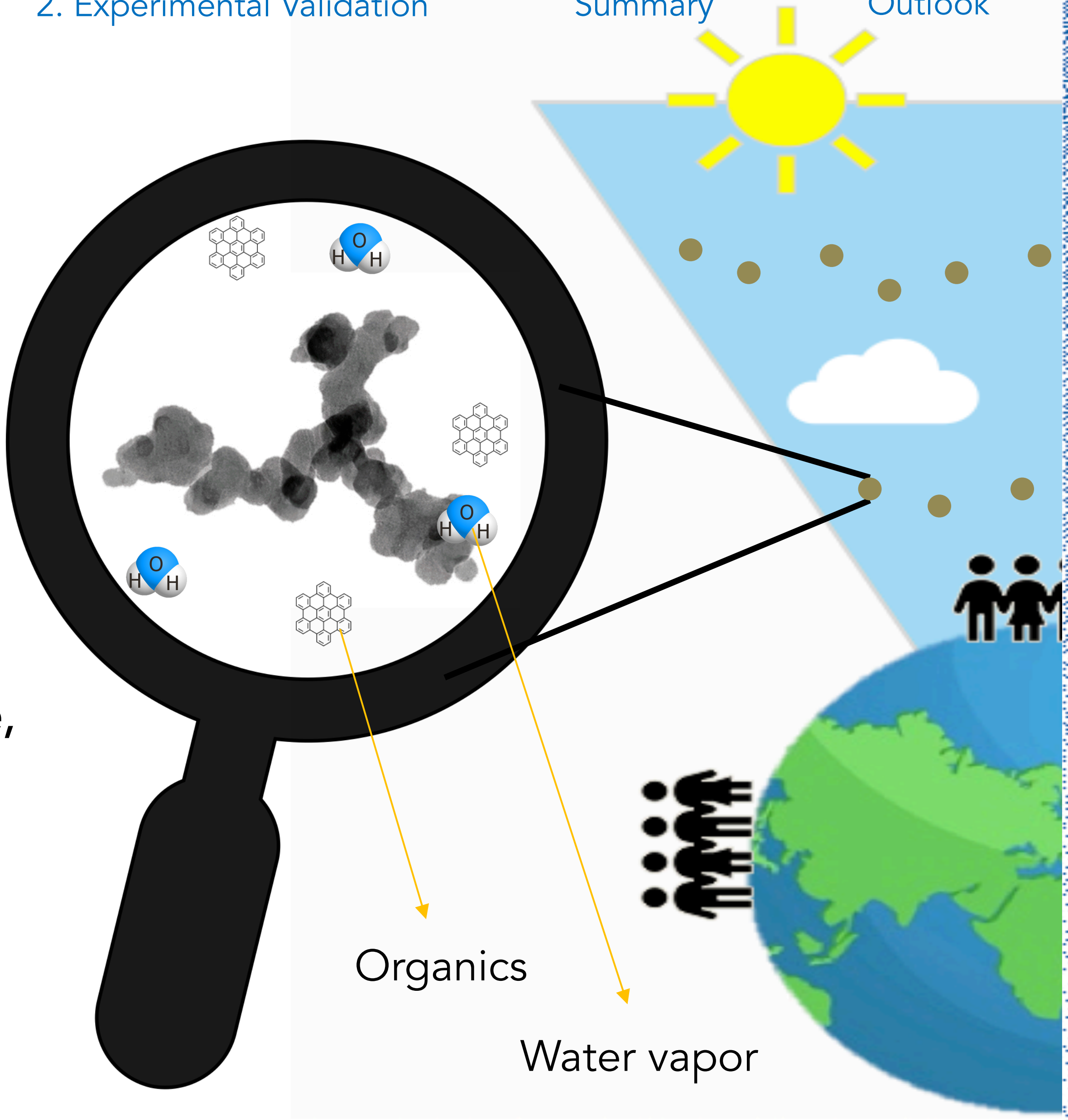
- BCFAs undergo various **modifications in shape, size and composition** after emission by:
  - Condensation of water vapour
  - Coating of organics
  - Aggregation process



Consequence of modifications in BCFAs

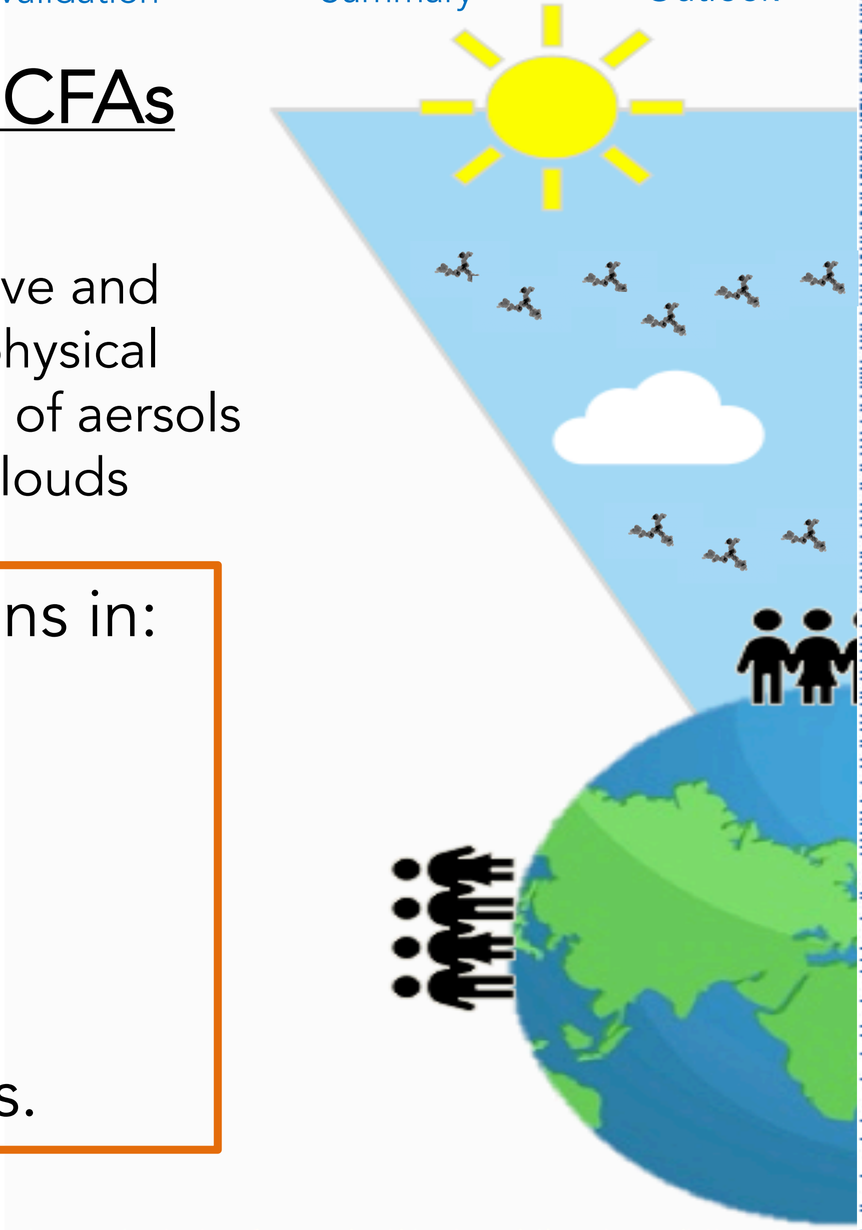
Modifications in BCFAs → Radiative and microphysical properties of aersols and clouds

Modifications in BCFAs → Influences BCFA optical properties

We are interested to quantify how modifications in:

- ❖ Size
- ❖ Morphology
- ❖ Composition

of BCFAs influence their optical properties.



Modifications in Black Carbon Fractal Aggregates (BCFAs)

❖ Size

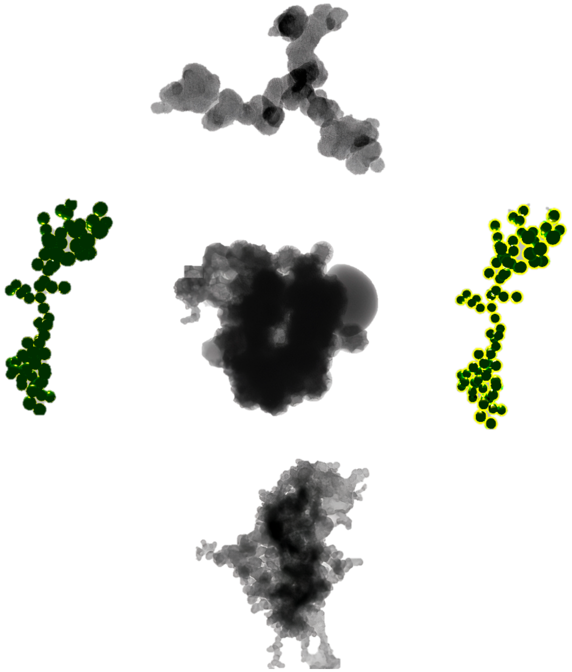
- Mobility diameter (D_{mob}) $\gtrsim$ 2 D_{vol}
- Volume equivalent diameter (D_{vol})
- Primary particle radius (R_{pp})

❖ Morphology

- Fractal dimension (D_f)

❖ Composition

- Volume fraction of Organics ($f_{organics}$)



The modifications can be studied by simulating various cases and modelling their optical properties

Ph.D. workplan

Goal: Investigate the modifications in BCFAs and their optical properties

Obj.1 — Modelling & parametrization

- Simulate BCFAs of various size, shape, or composition
- Quantify the changes in optical properties
- Parametrization scheme

Obj.2 — Experimental validation

- Laboratory generated soot:
  - Data for input parameters (size and composition)
  - Validation of modelled optical results

EURAMET EMPIR BLACK CARBON

Obj.3 — Optimized experiments

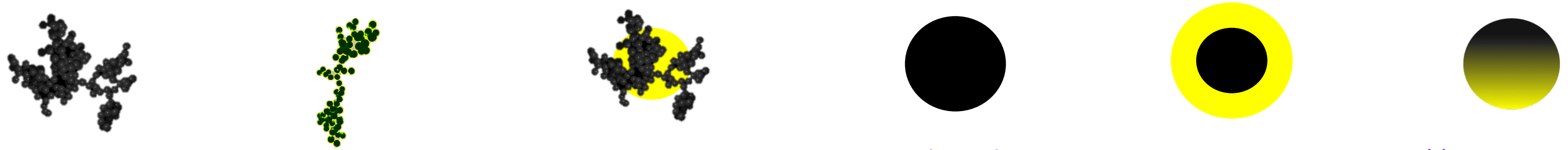
- In depth validation of optical modelling techniques

Introduction : 1. Modeling & Parametrisation

Optical modelling

↓

Key: Representation of BC particles



Aggregate | Coated aggregate | Aggregate + spherical coating | Single sphere | Coated sphere | Homogeneously mixed sphere

- ✅ Simulate lifecycle of BC particles (Dong et al., 2018; Ouf et al., 2016)
- ✅ Wide parameter space

↓

- ✅ Widely used
- ✅ Simpler
- ❌ Larger descrepancies (Wu et al., 2018; Adachi et al., 2010)

Modelling the optical properties of coated black carbon fractal aggregates (BCFAs) with changing size, morphology, and composition

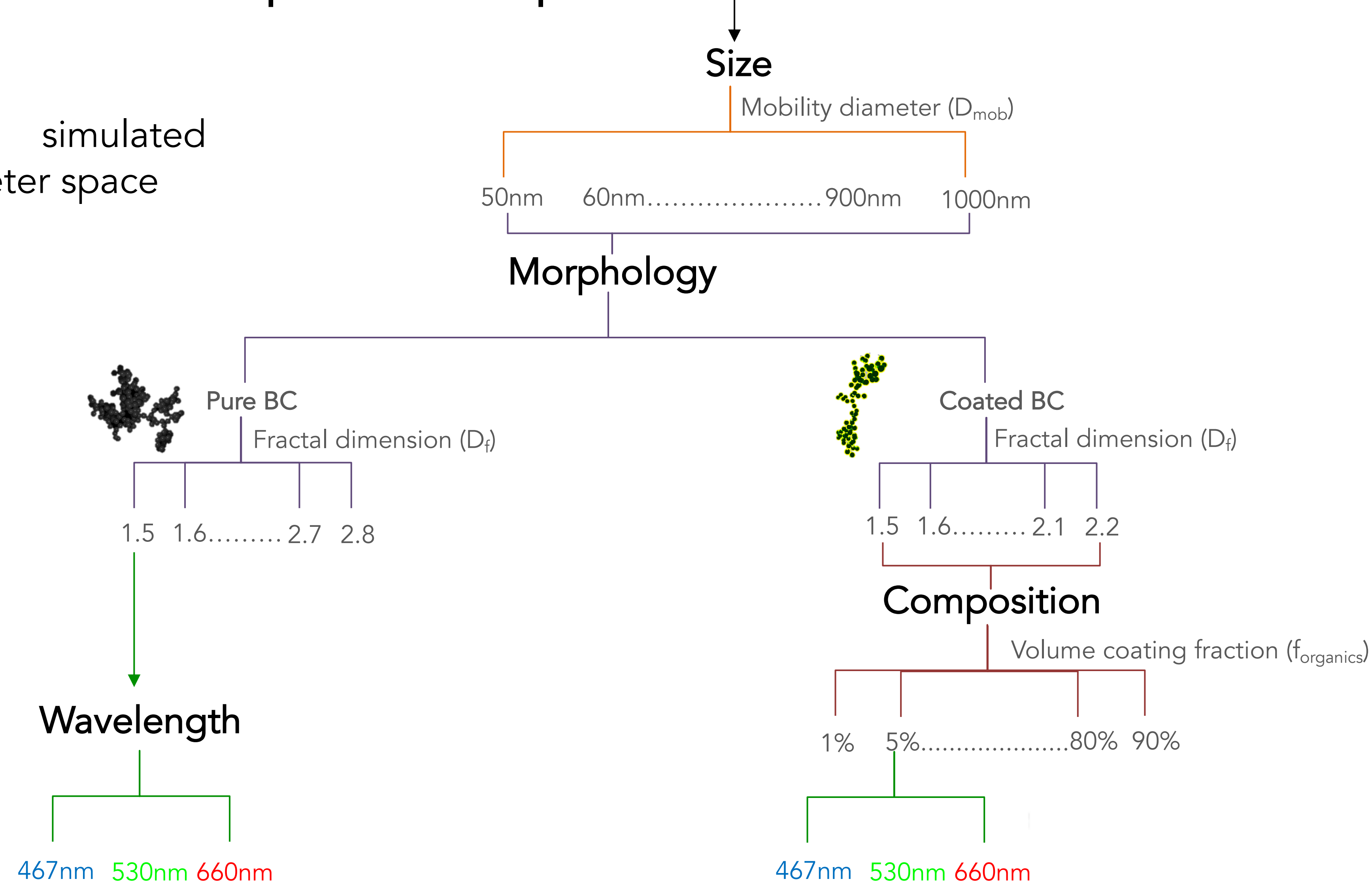
★ Wide parameter space of BCFAs.

★ Parametrization scheme for optical properties (extinction, absorption, and scattering).

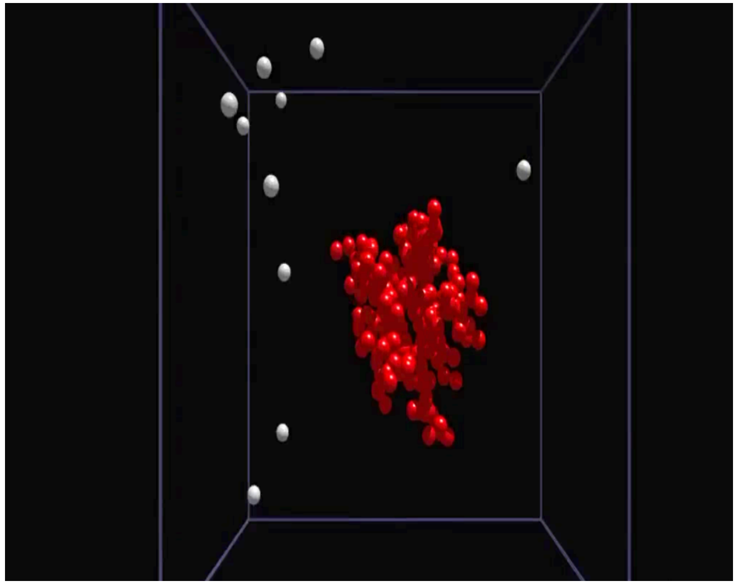
Wide parameter space of BCFAs

- The BCFAs are simulated following this parameter space

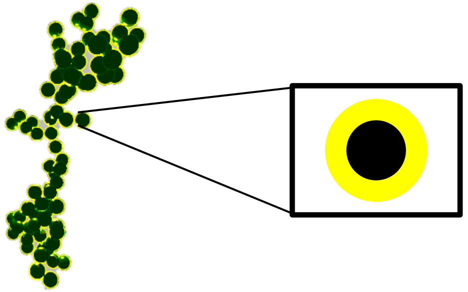
- Total of 192 cases.



Simulation of BCFAs



Tunable diffusion limited aggregation software to generate the black carbon aggregate simulations. (Woźniak, 2012)



- BC core of primary particle fixed to 15nm
- Increase the outer core size up to 30 nm according to the $f_{organics}$ %

Size of BCFAs

- Modelling studies use "number of primary particles" to represent size. (Smith and Grainger, 2014; Kahnert, 2010; Zhang et al., 2017)
- We used mobility diameter ⟶ conversion based on model by Sorensen, 2011.

Optical model

- Multi-sphere T-matrix Method (MSTM) used for modelling the optical properties.
  (Mishchenko et al., 2004)

- For reference:
  - Mie theory → volume equivalent sphere of the BCFA
  - RDG theory for absoption → $C_{abs}^{aggregate} = N_{primary\ particle} C_{abs}^{primary\ particle}$

Optical results

- Extinction, absorption, and scattering cross section ($C_{ext/abs/sca}$)
- Asymmetry parameter (g)
- Single scattering albedo (SSA)
- Mass absorption cross-section (MAC)
- Absorption Ångstrom Exponent (AAE)
- Absorption enhancement factor (E_λ)

Results: Changing morphology (D_f) of BCFAs

(A) Mass Absorption Cross-section MAC_{BC}

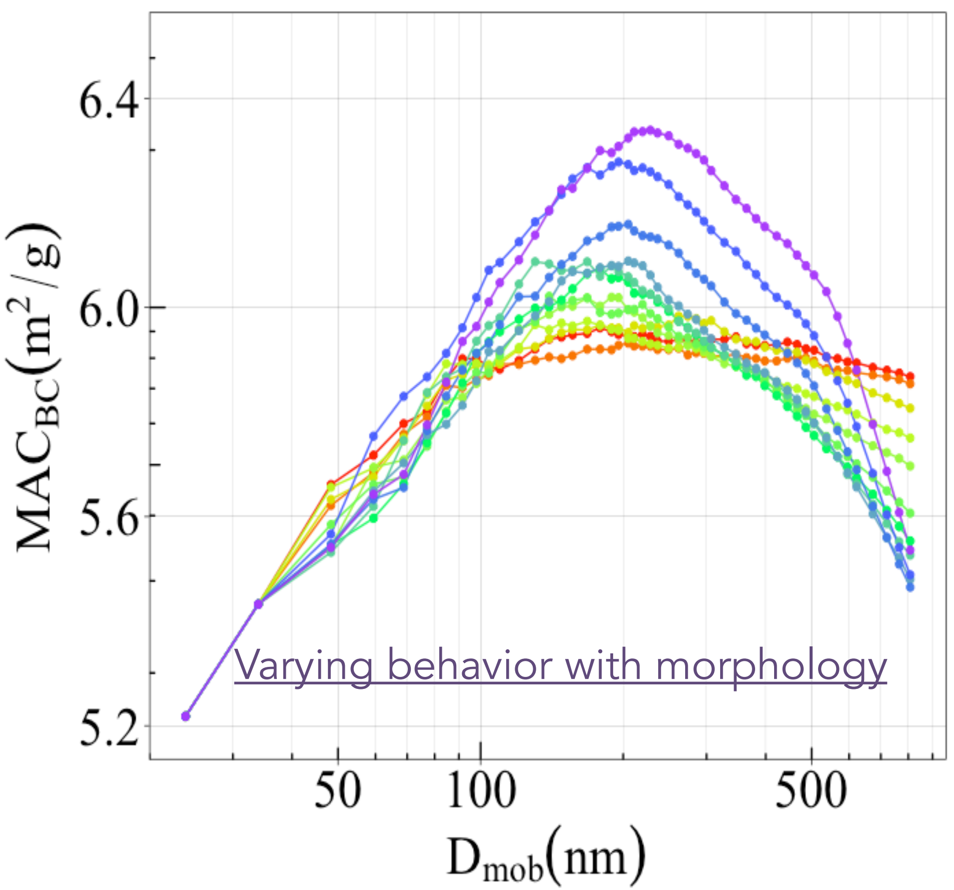
- Measure of probability of absorption
- Measured value of 4.55 to 18.5 m^2/g at 550nm.

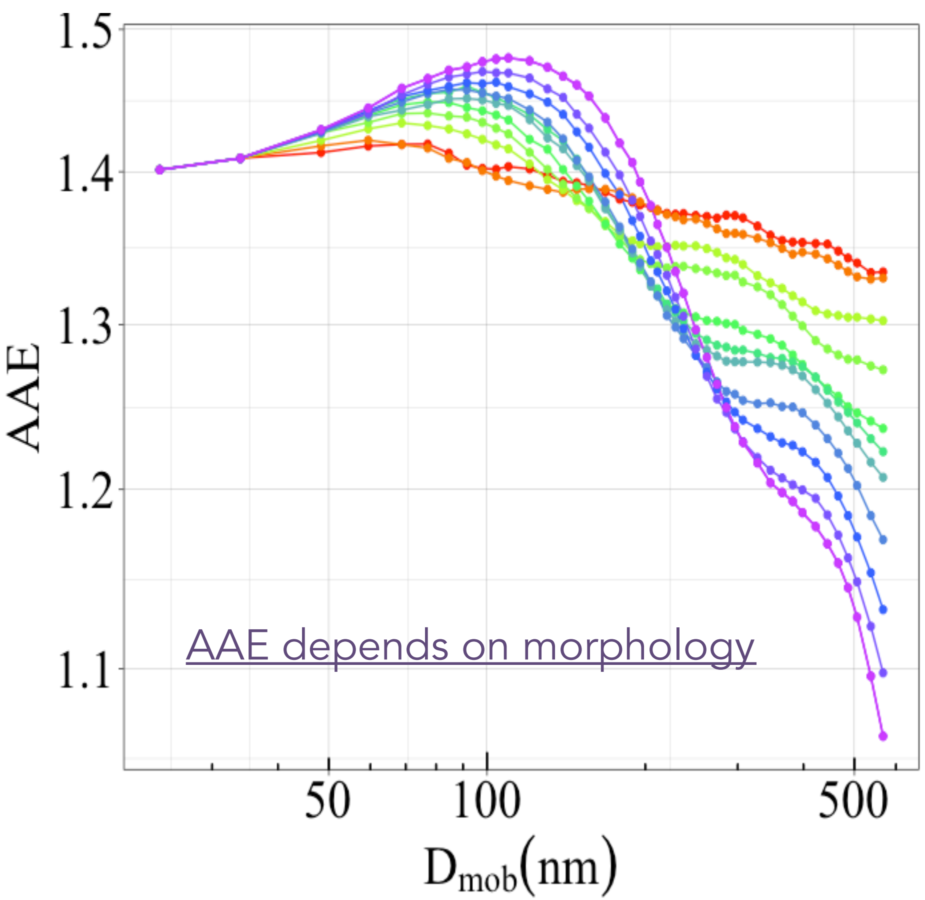
(Zanatta et al, 2016)

(B) Absorption Ångstrom Exponent AAE

- Slope of C_{abs} and λ ; spectral dependency; Proxy for composition.
- Measured value of 1.1 to 3.5 for diffusion flame generators.

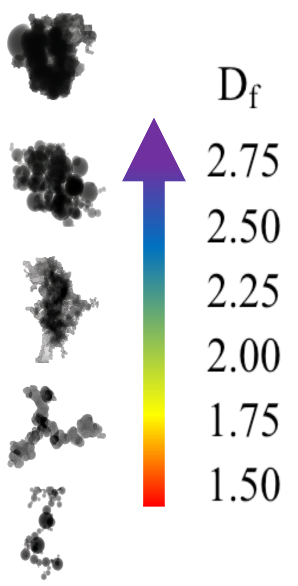
(Török et al., 2018)





Pure BC case

$f_{organics}$ = 0%



Results: Changing composition ($f_{organics}$) of BCFAs

(A) Mass Absorption Cross-section MAC_{BC}

- Measure of probability of absorption
- Measured value of 4.55 to 18.5 m^2/g at 550nm.

(Zanatta et al, 2016)

(B) Absorption Ångstrom Exponent AAE

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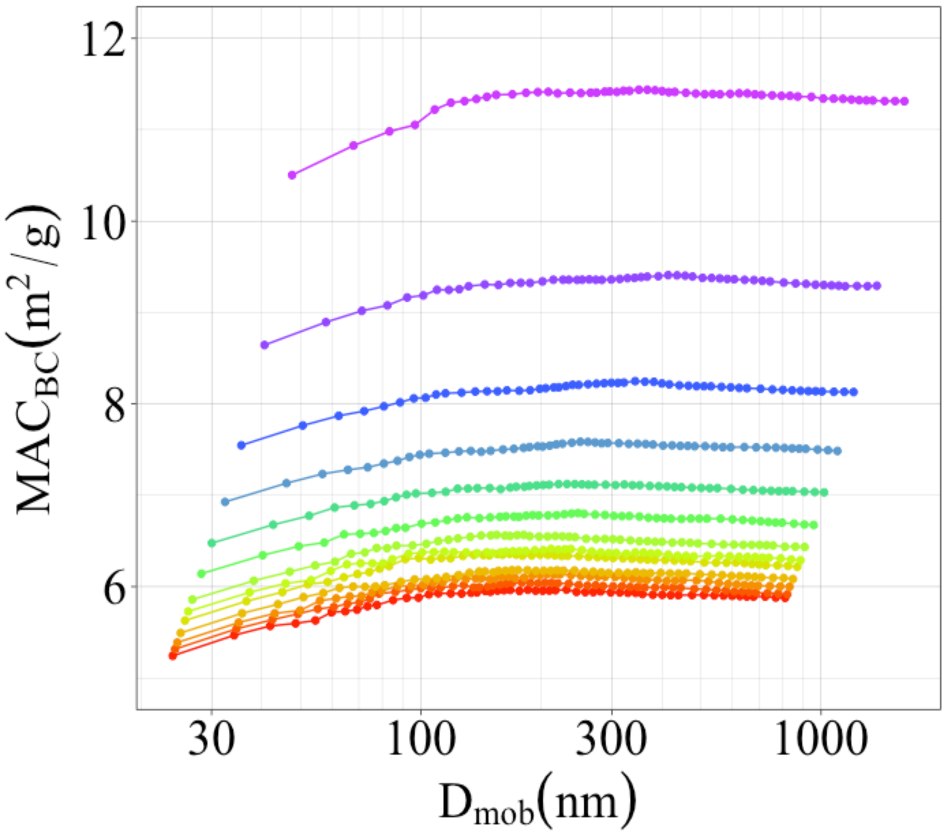
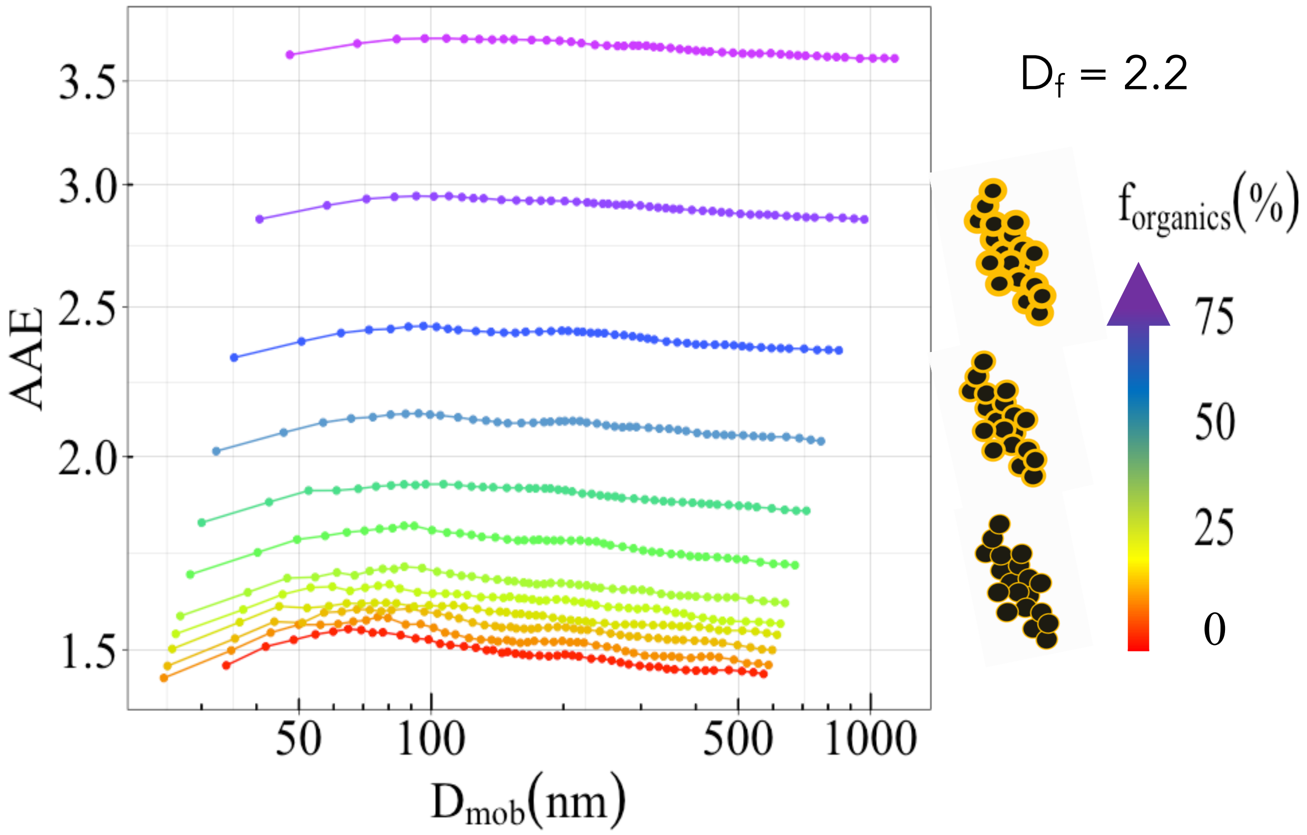




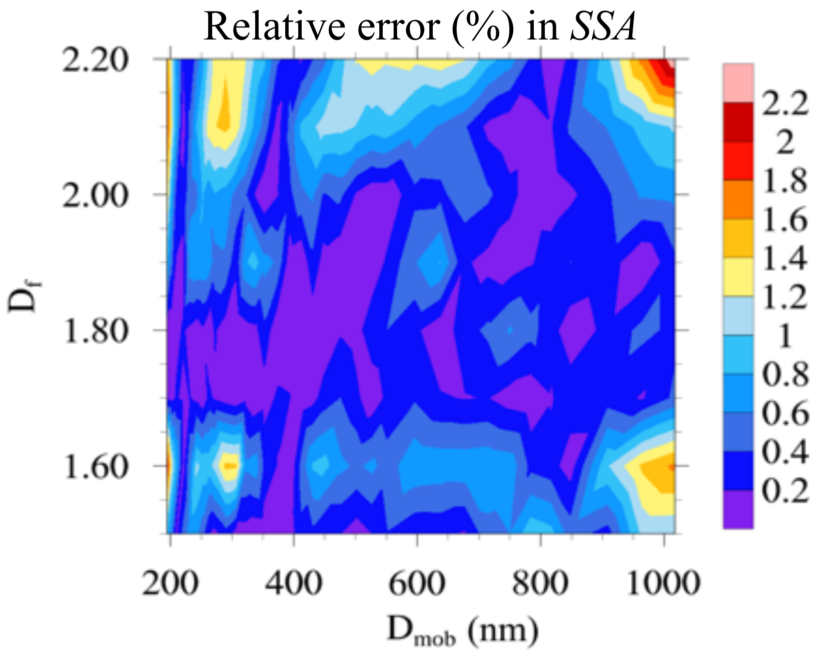
Message: Dependency on composition is straight forward, whereas a complex dependency on morphology

Parametrization scheme

- A parametrization scheme for optical properties of coated BCFAs w.r.t mobility diameter.
- Applicable for modelling, ambient and laboratory-based BC studies.

Example: Single Scattering Albedo $$lnSSA = k_0 + k_1 lnD_{mob} + k_2 \ln(lnD_{mob})$$

- k_0, k_1, and k_2 vary according to 192 sub-cases of morphology, composition, and wavelength.



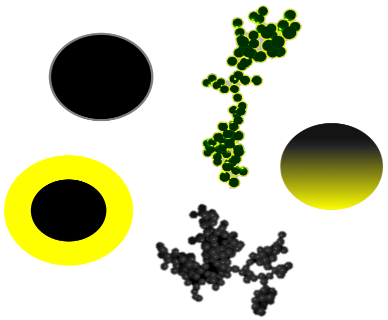
Sub-case:
$f_{organics}$ =50%
λ = 660nm
D_f = 1.5 to 2.2

Error Analysis

$$\text{Relative Error \%} = \frac{|SSA_{optical\,model} - SSA_{parametrisation}|}{SSA_{optical\,model}} \times 100$$

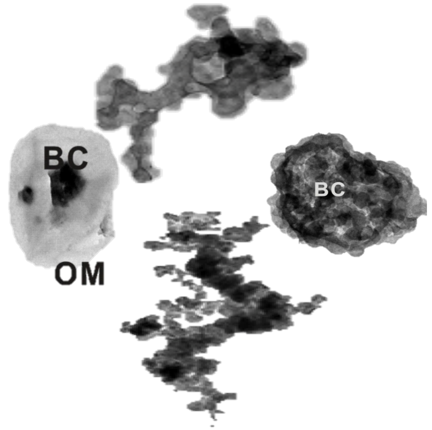
Optical property	Relative Error (%)
Cross-sections	<2
SSA	<3
g	<18
MAC	-
AAE	-

2. Experimental validation : Introduction



SOOT MODEL

How representative are these soot models with respect to laboratory/ambient measurements?



LABORATORY/AMBIENT

Optical modelling studies of soot:
Liu et al., 2015; Smith and Grainger, 2014; Kahnert 2010; Zhang et al., 2017.

Optical instruments:
Aethelometers, Nephelometers, Cavity Attenuated Phase Shift extinction (CAPS PMex) monitors, and Multi Angle Absorption Photometer (MAAP).

Obj. 2: Laboratory generated soot for validation of optical modelling techniques

Methodology

EURAMET EMPIR BLACK CARBON

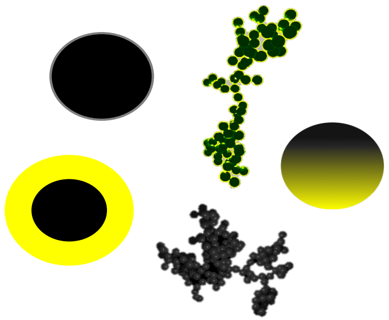
LABORATORY CAMPAIGNS

Soot generators

- mini-CAST
- Inverted flame generator
- PALAS spark generator
- Fullerene soot

MPSS - Particle size measurements

EC/OC analysis - composition measurements



SOOT MODEL

AE33, MAAP, Nephelometer

CAPS PM_{ex660}, CAPS PM_{ex530}, CAPS PM_{ex450}

OPTICAL PROPERTIES

Validation

Modelling approaches

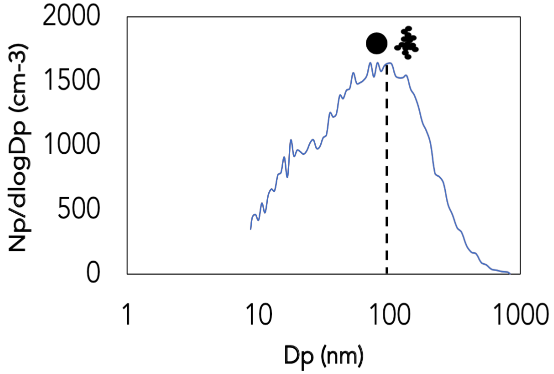
BC model

- Various BC representation models were used

Single sphere | Coated sphere | Homogeneous mixed sphere | Aggregate | Coated Aggregate | Aggregate with spherical coating

Particle size

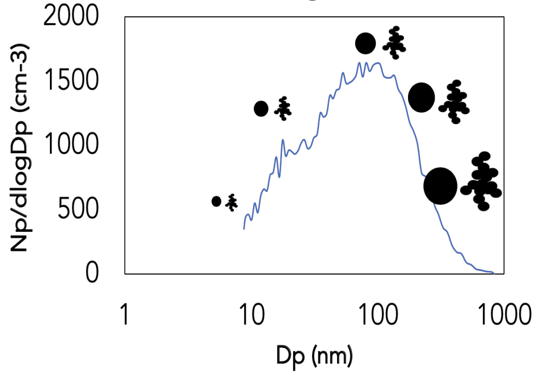
NSD or VSD



Point approach: optical results at the mean mobility diameter of the number or volume size distribution.

or

BULK



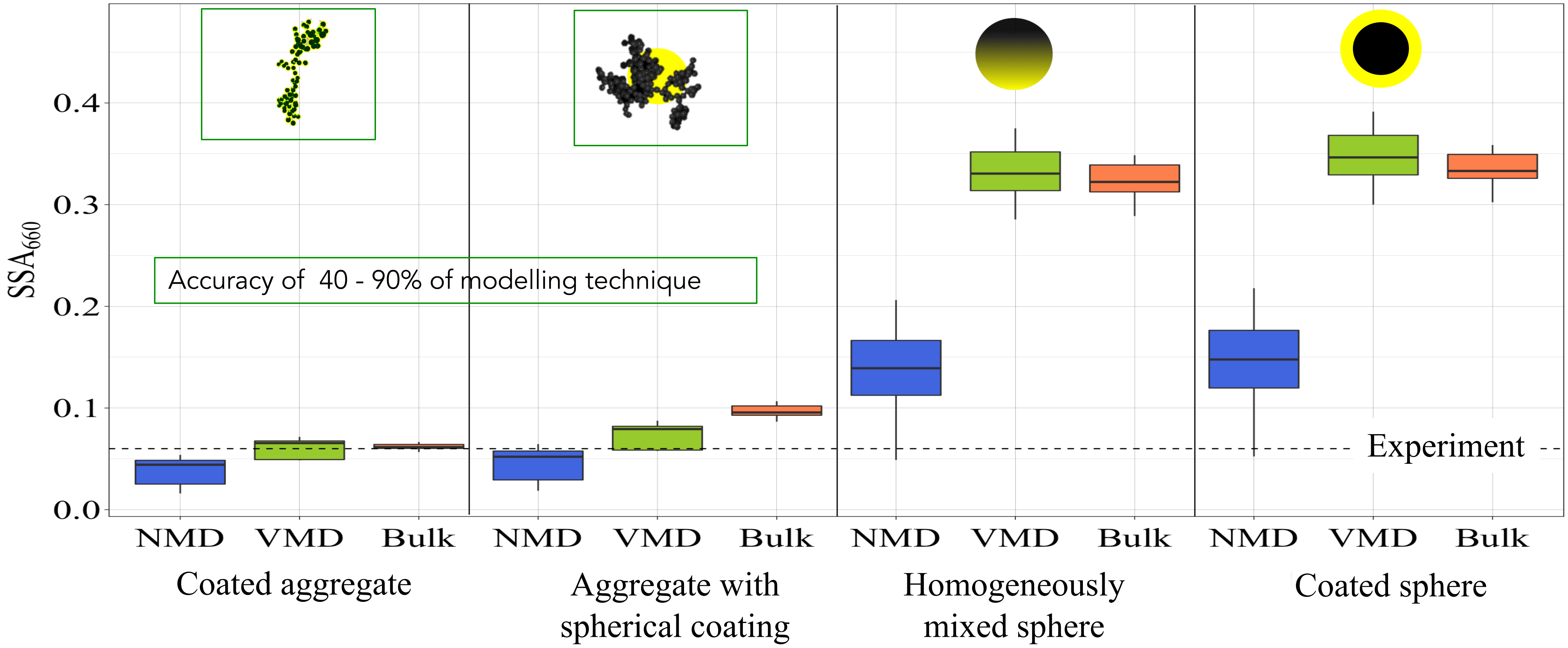
Bulk approach: optical results integrated over entire number size distribution.

NMD = 129nm
VMD = 181nm
EC/TC = 0.68

Experimental SSA vs modelled SSA

mini-CAST
5201BC

Ideal case (low organic content)

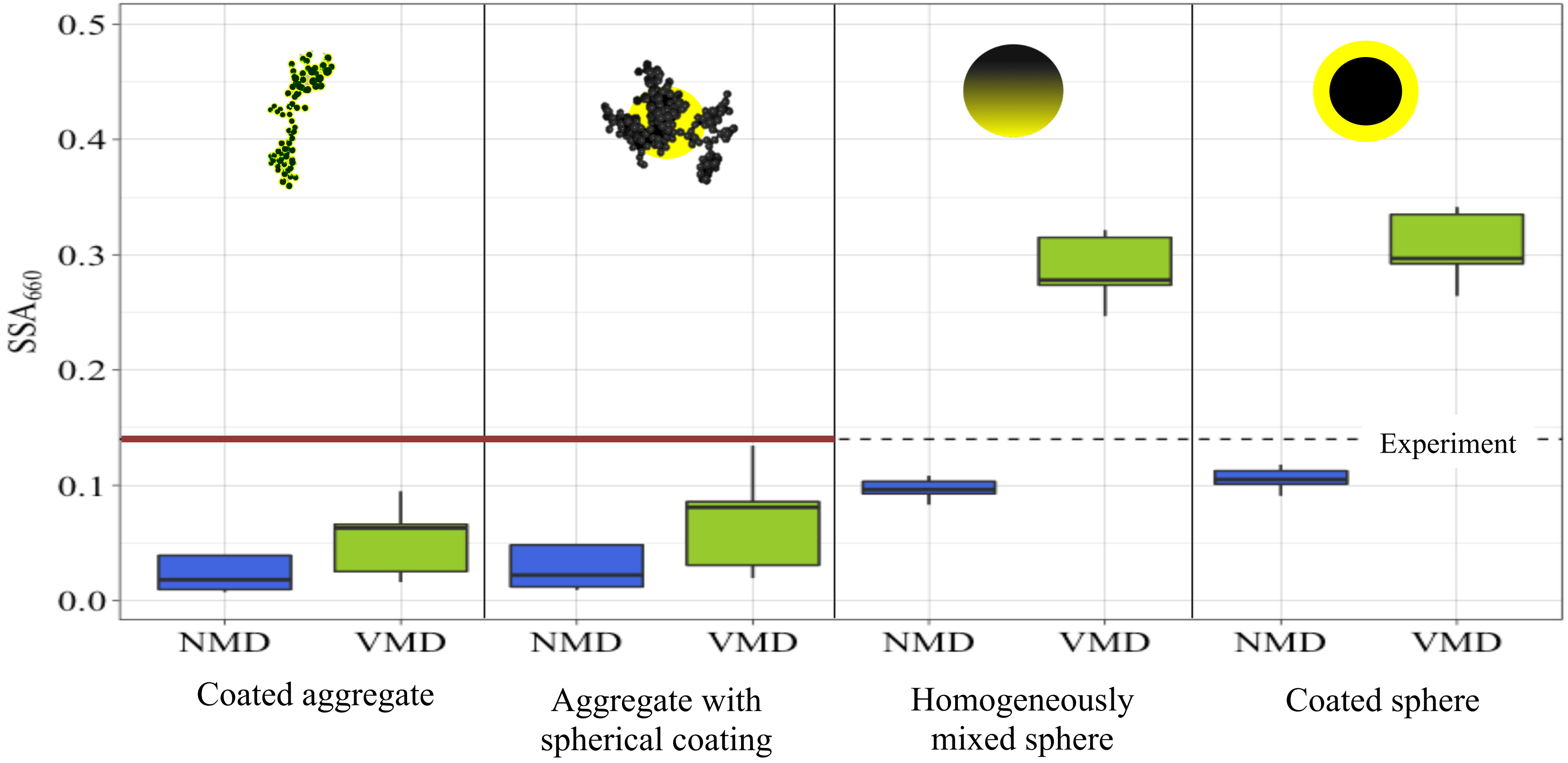


Experimental SSA vs modelled SSA

NMD = 112nm
VMD = 157nm
EC/TC = 0.55

mini-CAST 5203C

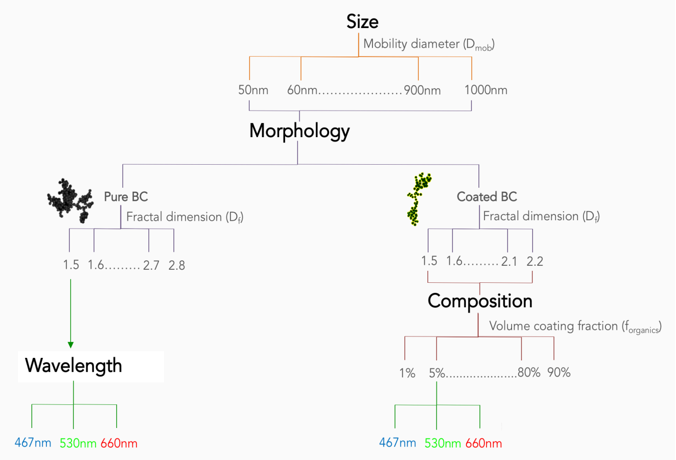
Case of higher organic content



- In this case, the aggregate representation underestimates the SSA
- Morphology might be different than the expected literature value of D_f = 1.7 for freshly emitted soot.

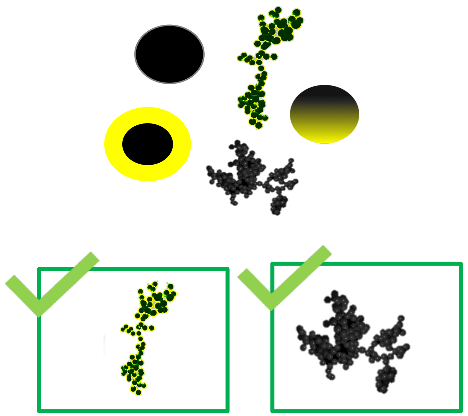
Summary

1. Modelling & parametrisation



- ❖ Optical properties of BCFAs were investigated as a function of particle size (D_{mob}), morphology (D_f), composition ($f_{organics}$), and wavelength (λ)
- ❖ Parametrization scheme for BCFAs optical properties was developed, applicable for modelling, ambient and laboratory-based BC studies.

2. Experimental validation



- ❖ Modelling techniques are validated with their experimental equivalent results.
- ❖ For the low organics case, aggregate representation match to the experimental values, with an accuracy ranging between 40 – 90%.

Outlook

- Optical modelling of BC particles can be a key tool in reproducing laboratory or ambient optical measurements.
- Finding the best representation of BC particles for optimal modelling results can be challenging due to complex changes in their morphologies.
- Optimized laboratory experiments must be conducted to reduce the discrepancies in modelled optical properties:
  - In addition to present size and composition measurements:
    - Estimates of fractal dimension (morphology) $\Longrightarrow$ DMA-CPMA system
    - Estimates of primary particle size $\Longrightarrow$ TEM analysis

Improvement in accuracy

Ph.D. Progress

Goal: Investigate the changes in BCFAs and their optical properties

Obj.1 – Modelling & parametrisation

- Status : *Completed*
- *Paper submitted in ACP*

Obj.2 – Experimental validation

- Status : *Further analysis of results*
- *Romshoo et al. 2020, EAC poster (First winner, BPA 2020).*

Obj.3 – Optimized experiments

- Status : *Experiment to be conducted by mid of 2021.*

Thank you! ☺