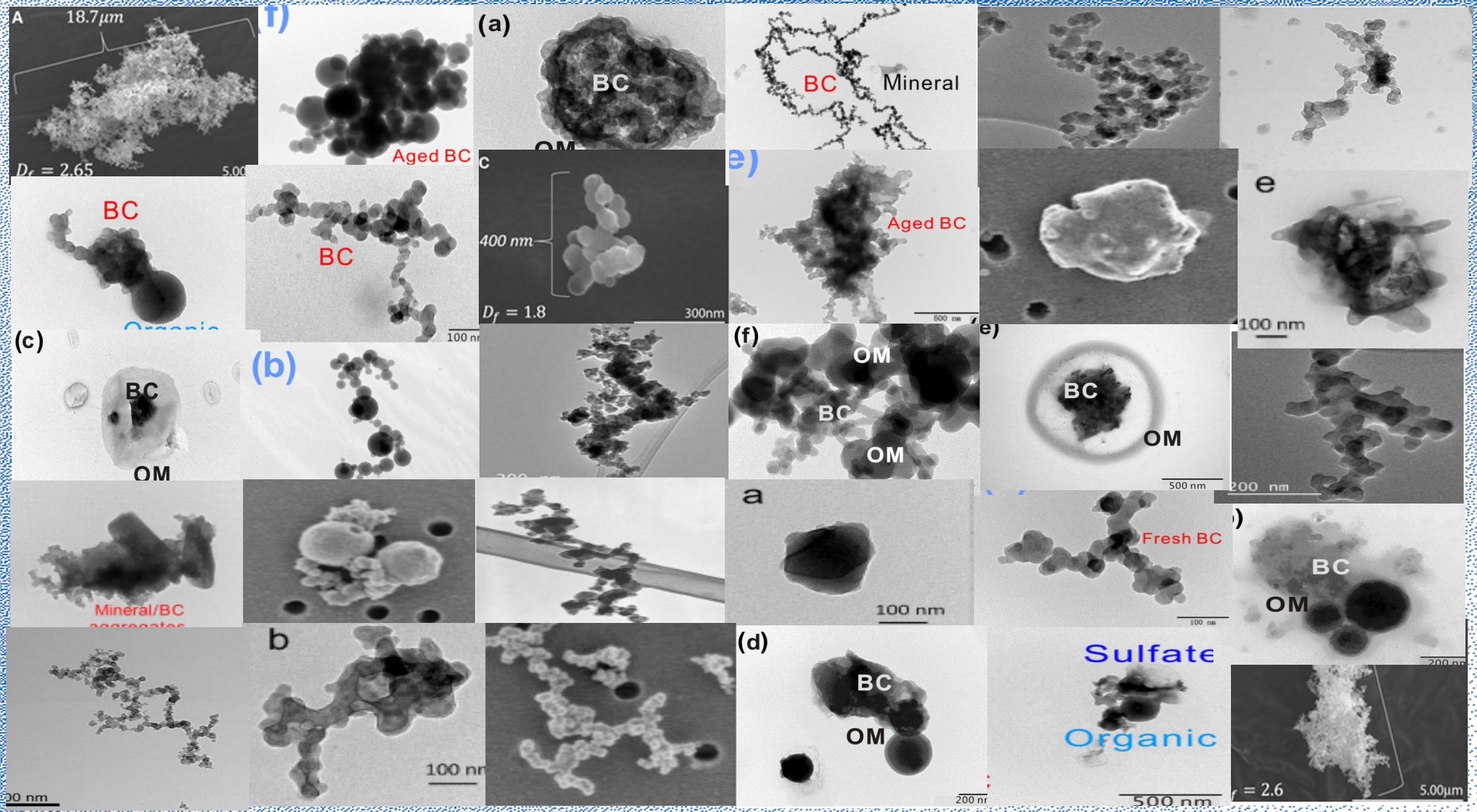
A
18.7μm
D_f = 2.65
5.00
(f)
Aged BC
(a)
BC
OM
BC
Mineral
BC
BC
Organic
c
400 nm
D_f = 1.8
300nm
e)
Aged BC
100 nm
e
(c)
BC
OM
(b)
(f)
OM
BC
OM
e)
BC
OM
500 nm
200 nm
Mineral/BC
a
100 nm
Fresh BC
BC
OM
b
100 nm
(d)
BC
OM
200 nm
Sulfate
Organic
500 nm
= 2.6
5.00μm

Experimental and Modeling Study of Optical Properties of Black Carbon with Organics

Baseerat Romshoo

First Ph.D. Talk

15/08/2019

Supervison Committee : Prof. Dr. Alfred Wiedensohler, Dr. Thomas Müller & Dr. Laurent Polain.

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

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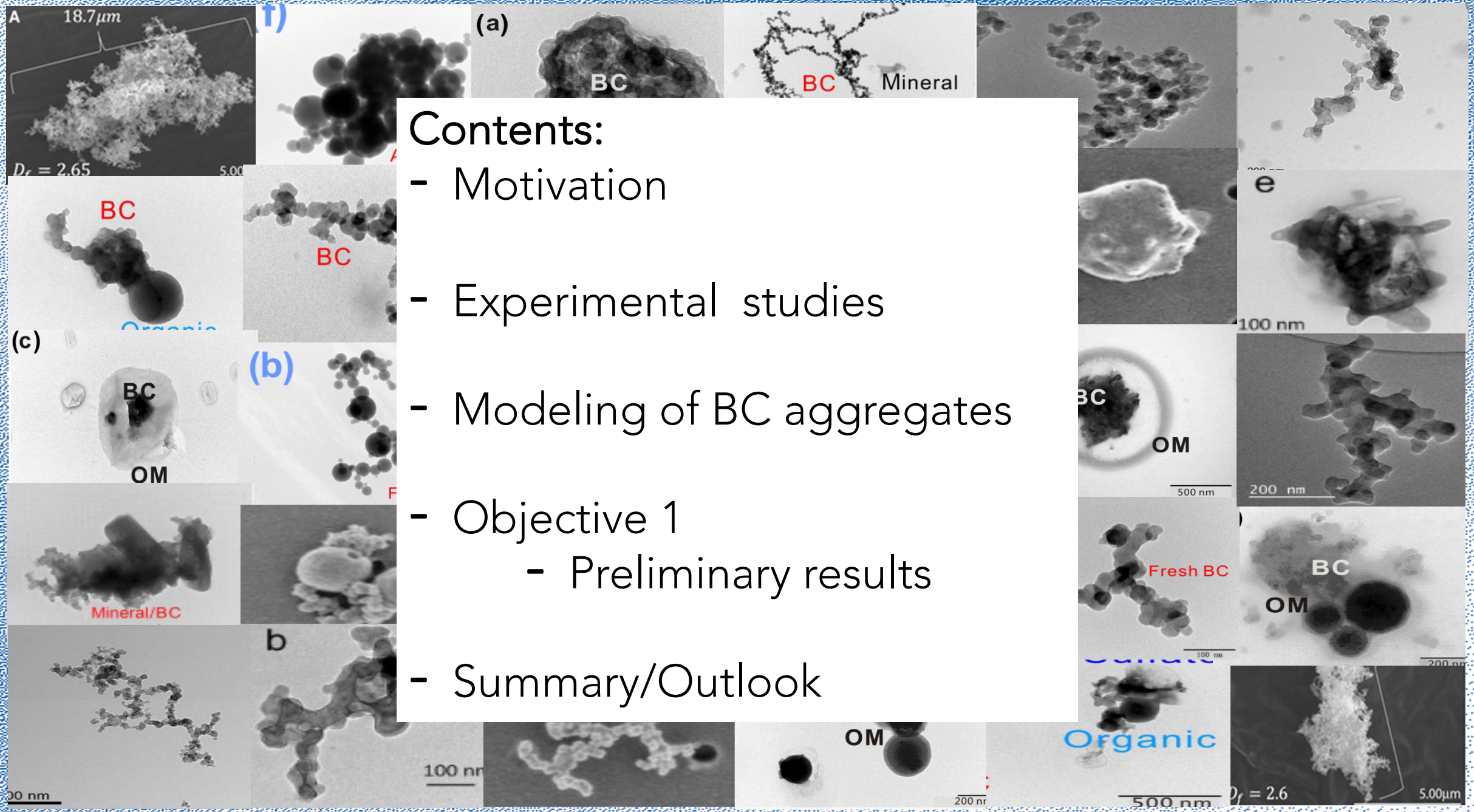


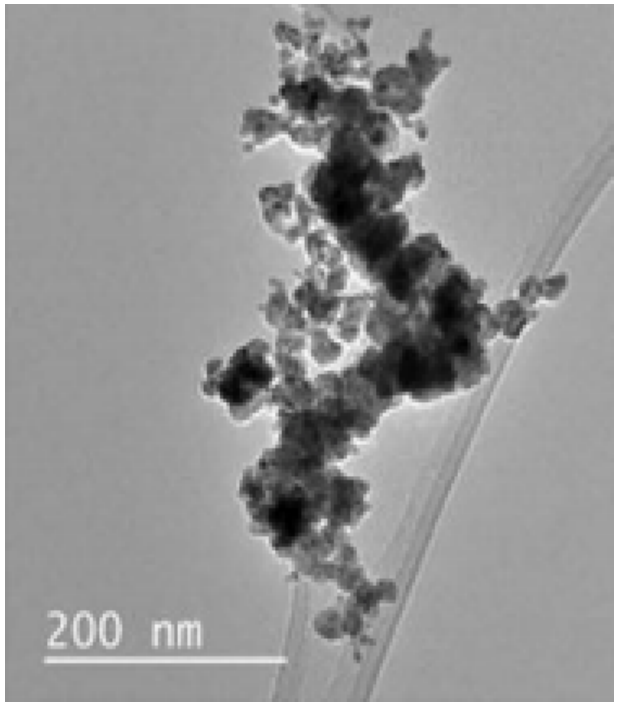
Contents:

- Motivation
- Experimental studies
- Modeling of BC aggregates
- Objective 1
  - Preliminary results
- Summary/Outlook

Black Carbon?

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

- These particles are **highly absorbing** solar radition.



Lie et al., 2008.

SOURCES

Traffic

Cooking

Power Plants/ Industries

Bio-mass burning

Google.

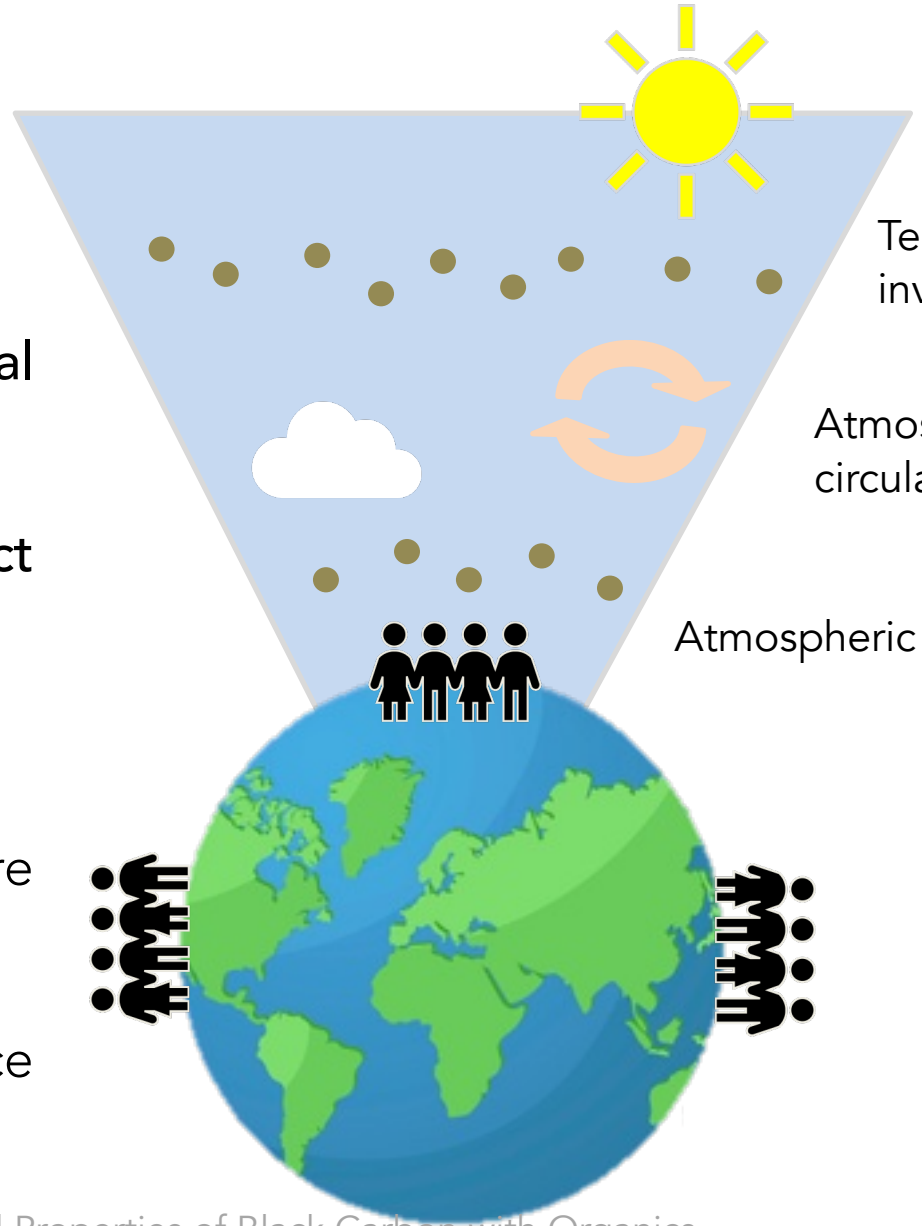
Impacts of Black Carbon

I. Climate

- Radiative and dynamic effects.
- Second largest contributor **for global warming (IPCC 2007)**
- Clouds - **direct, semi-direct and indirect effects**.

II. Eco – System and Human Health

- Harms **human health** and cause premature deaths (Jansen et al; 2011).
- Accelerate melting of snow and sea ice (Dong et al; 2018).



Soot?

Black, blackish or brown substance formed by combustion.

Black Carbon / C_{Soot}

Purely carbon, minor amounts of hydrogen and oxygen.

Organic Carbon

Co-emitted particles during combustion.

Light Absorbing Carbon (LAC)

Brown Carbon

Light absorbing part of organic carbon. For eg, Tarr.

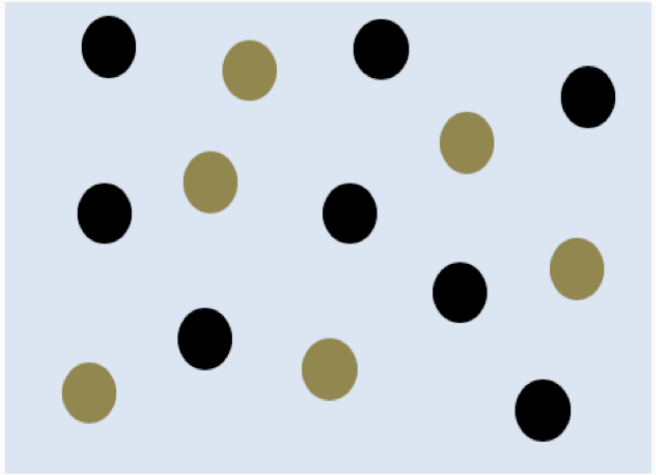
Organics?

- In the atmosphere, organics is present along with BC.
- Constitute co-emittants ⟹ Polyaromatic hydrocarbons (PAHs)
- High flame equivalence ratio (i.e. more fuel, less oxygen) ⟹ More organics

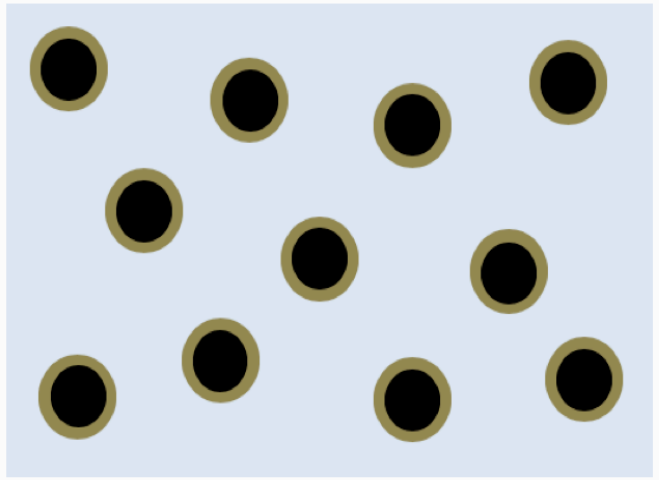
Organics are **Internally or Externally Mixed** with Black Carbon :

My focus

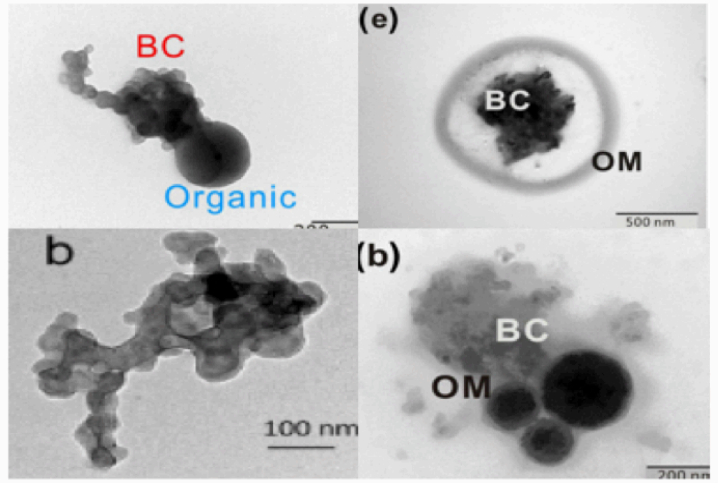
Externally Mixed



Internally Mixed (As Coating)



Internally Mixed (In Real)

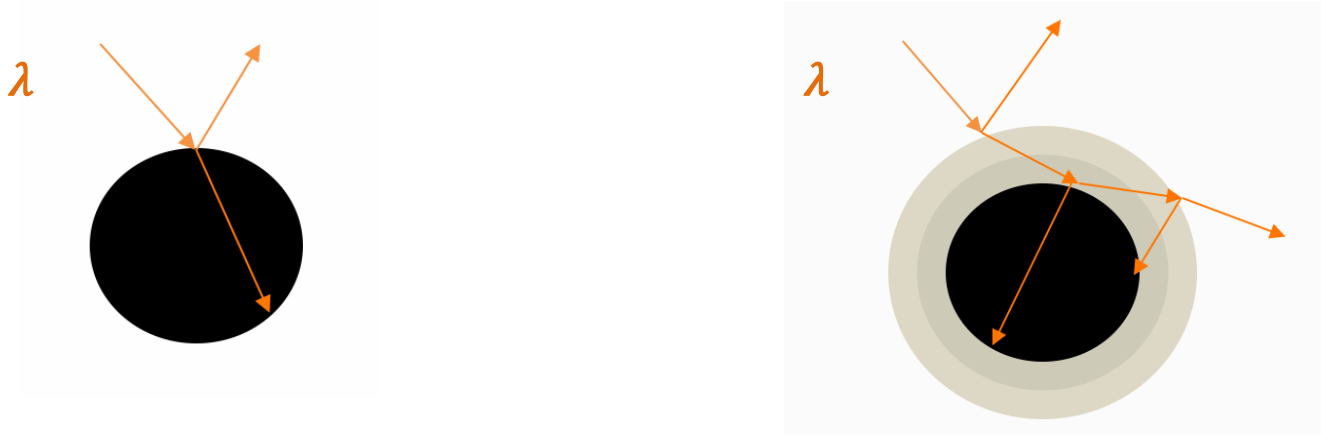


Dong et al., 2018.

Property of BC coated with organics

- When organics are internally mixed with black carbon:

  i. Enhance light absoption of black carbon due to a "lensing effect".



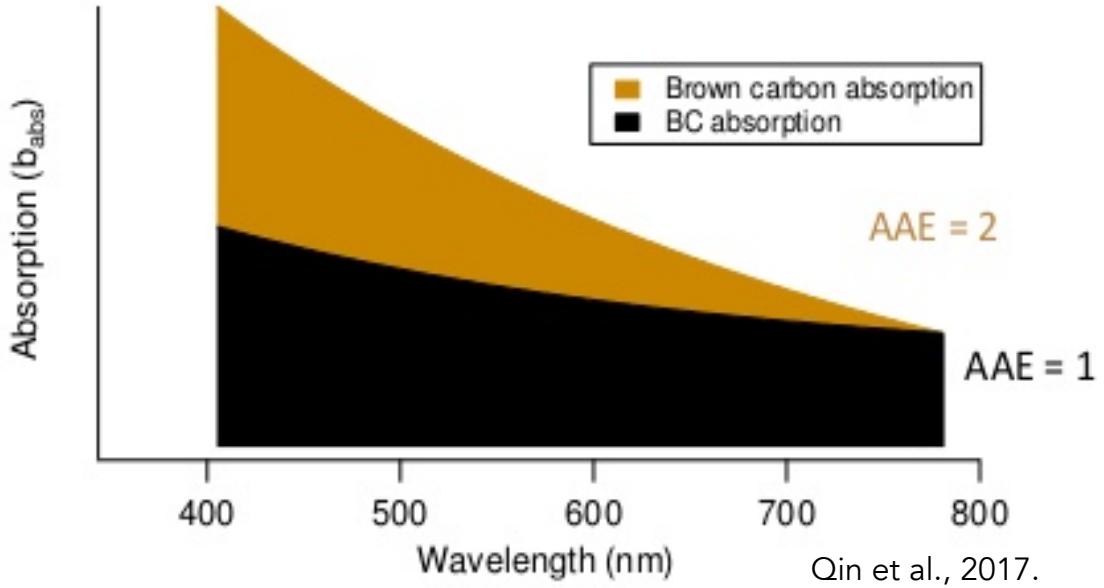
  ii. Modify the hygroscopicity of black carbon.

This is the reason we need to study internally mixed black carbon and organics.

Optical Properties (OP)

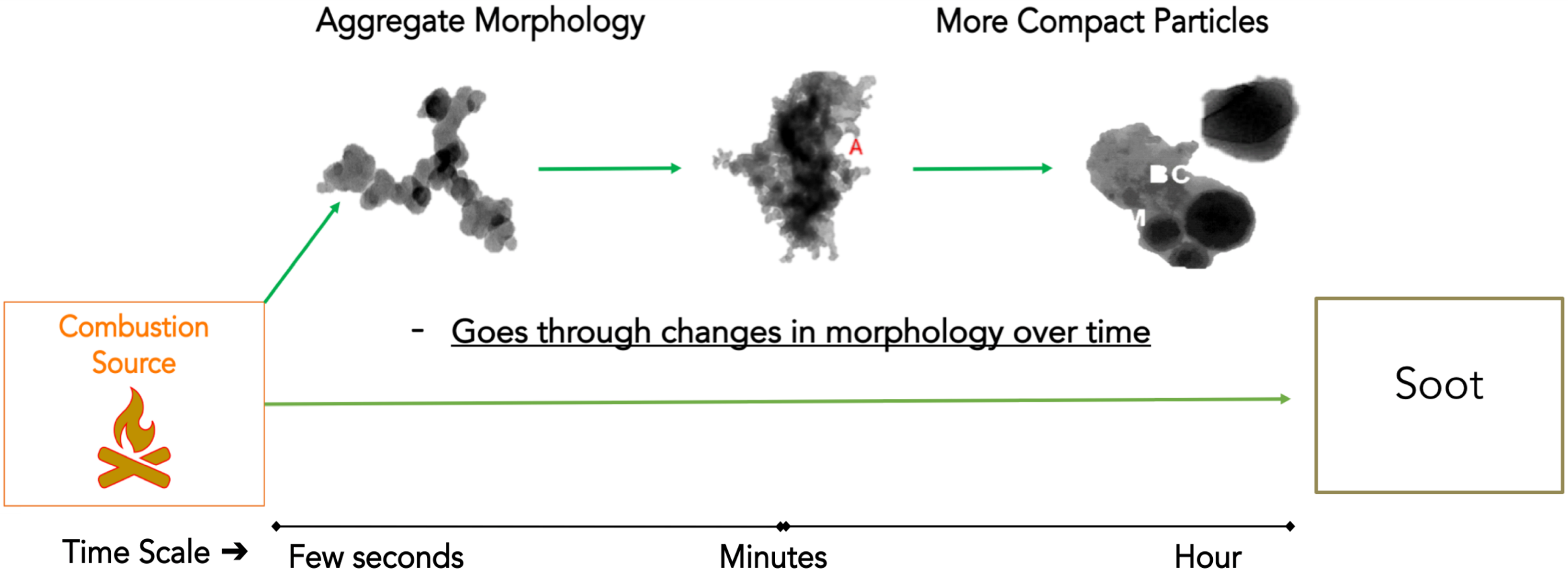
How to measure this enhancement in absorption?

- OP 1. Mass Absorption Cross – Section (MAC) = Absorption per unit mass.
- *MAC_{BC} = 4 – 6 m^2/g (Bond et al., 2006).*
- *$MAC_{BC\ with\ organics}$ = 7-10 m^2/g (Cappa et al., 2012)*
- OP 2. Single Scattering Albedo (SSA)
  = Scattering/(Absorption + Scattering)
- OP 3. Angstrom Absorption Exponent (AAE)
  Slope of Absorption vs λ



Qin et al., 2017.

How do BC particles look like?



- Experimental & modeling study ⟹ early stages of formation

- Understand the micro-physics during the transition stages

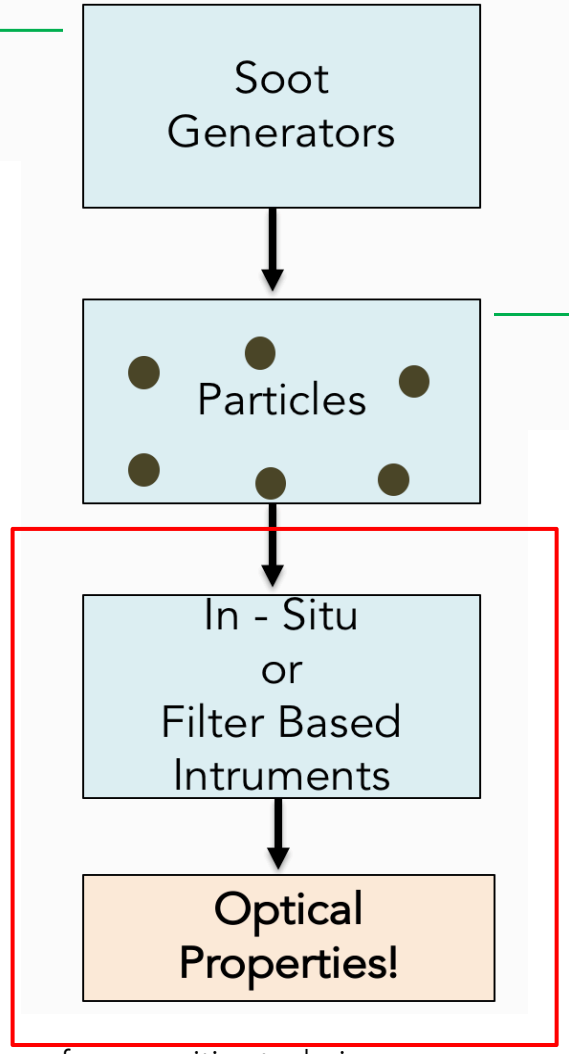
Overview of prev. laboratory studies

Studies by :
Moore et al, 2014.
Mamakos et al, 2013.

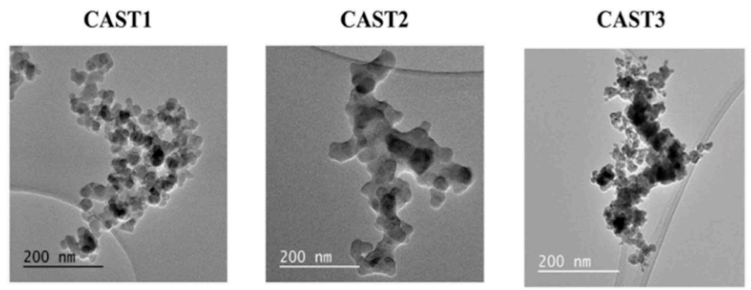
- Mapped the operation of combustion based generator.
- BC mode size, concentration, and OC fraction can be adjusted by varying the burner flow rates.

1.Reproducibility of generator

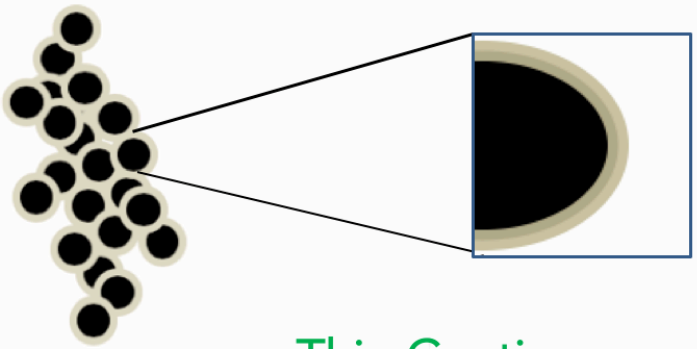
2.Study of optical properties



Study by :
Ouf et al 2016.



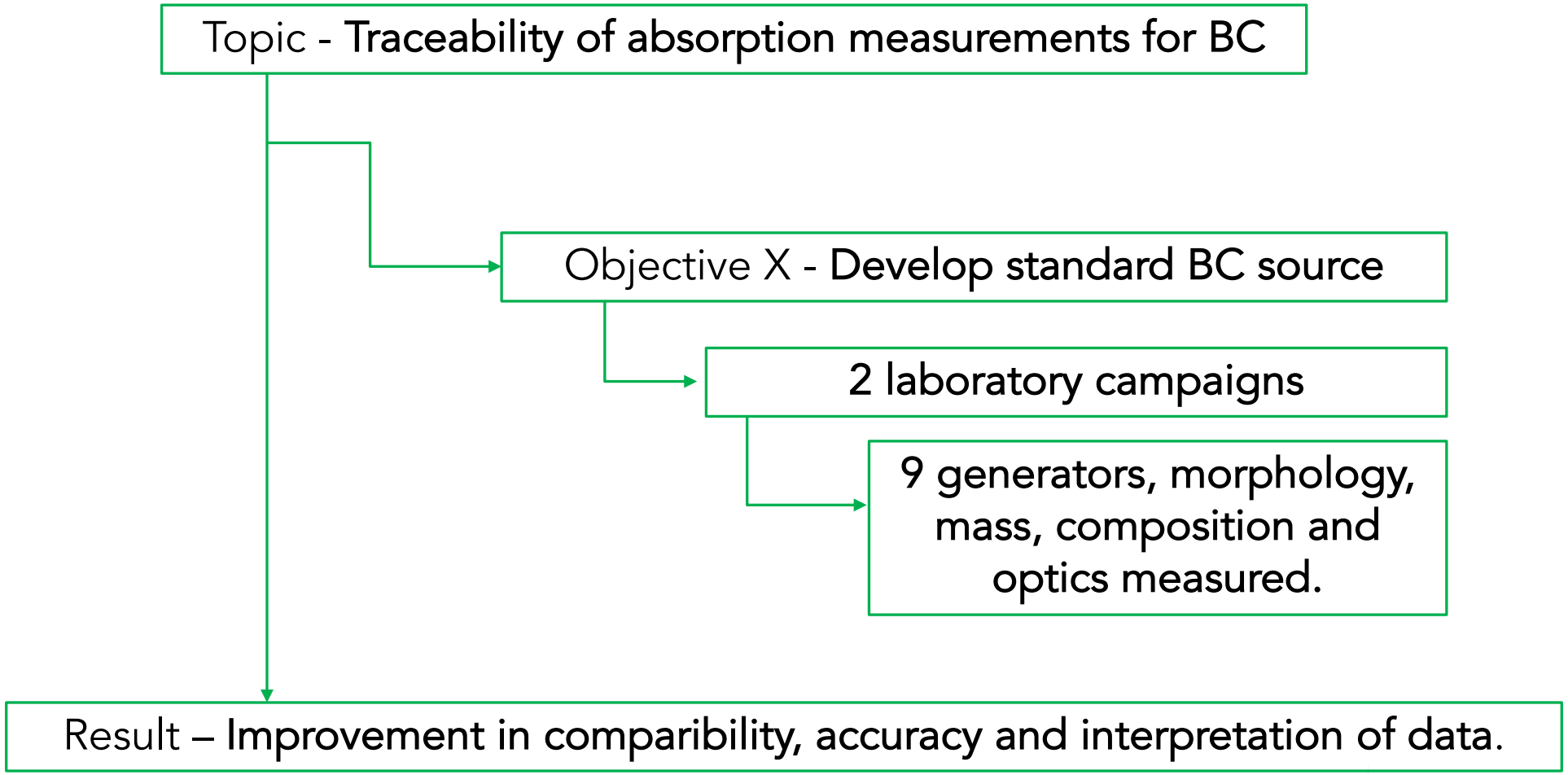
- Evidence[1] of organics attached to edge of graphite crystallites.



Thin Coating

[1]Using Near Edge X-ray Absorption Fine Structure (NEXAFS) - surface-sensitive technique.

EMPIR Black Carbon Project



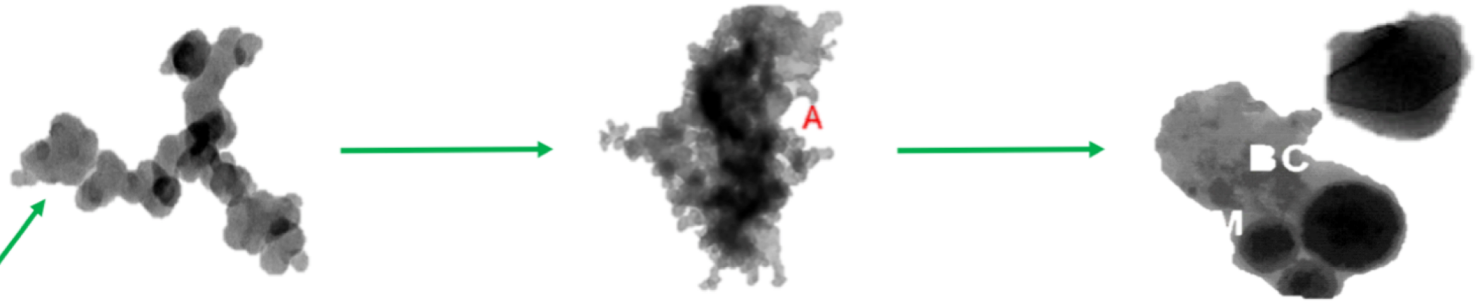
How do BC particles look like?

Fractal Aggregates

My Focus

Aggregate Morphology

More Compact Particles



Combustion Source

- Goes through changes in morphology over time

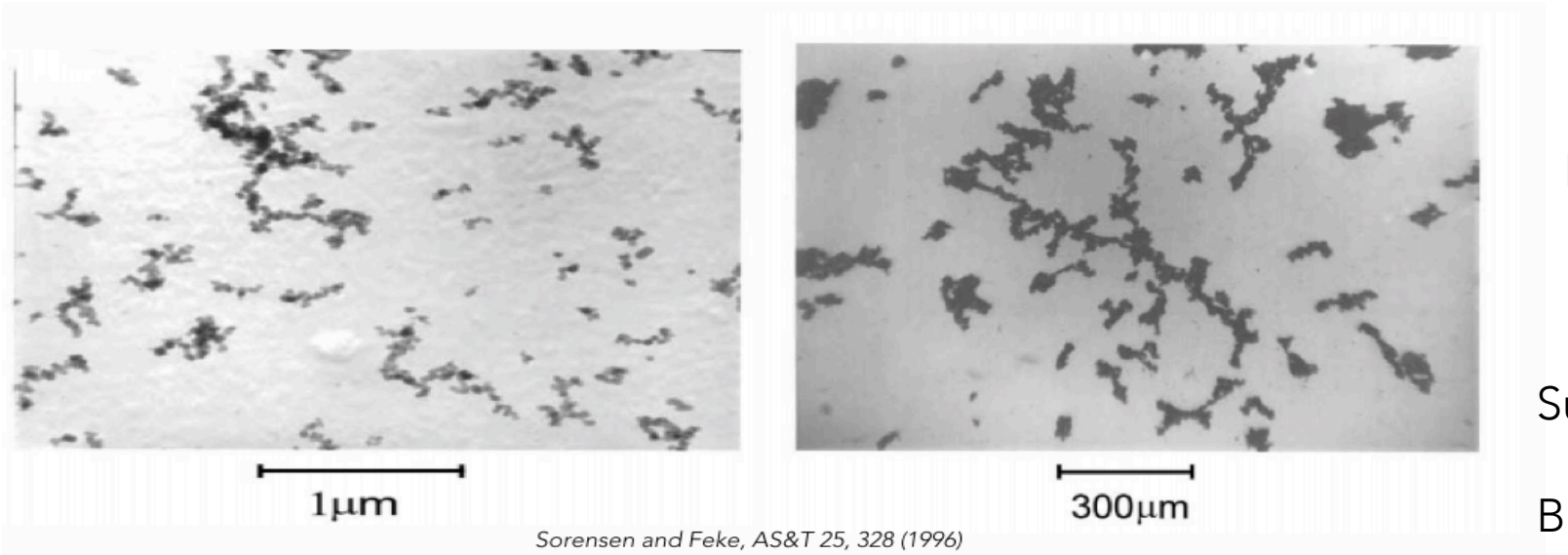
Soot

Time Scale ➔ Few seconds Minutes Hour

- Experimental & modeling study ⟹ early stages of formation

- Understand the micro-physics during the transition stages

Fractal Aggregates



Sorensen and Feke, AS&T 25, 328 (1996)

Similar shapes.

Now, note the scale bars.

← Scale Invariance

Such objects ➤ Fractals

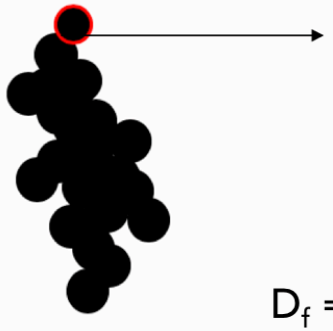
Black Carbon ➤ Fractal Aggregate

(Mandelbrot 1977)

← Diffusion Limited Aggregation (DLA)

Wozniak et al, in 2012 developed a software based on DLA to generate aggregates

Properties of aggregate



Primary Particle

a = Radius of a primary particle

- **Radius of primary particle (a)**
  It is a function of the source.
- Number of Primary Particles (N_s)
- **Fractal Dimension (D_f)**
  Measure of compactness of the particle
  Function of residence time.

D_f = 1.7

D_f = 2.2

Linking aggregate properties to size measurements? = **Power Law** (*Park et al, 2004*)

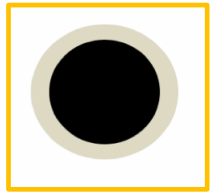
Mobility Diameter

$$N_s = k' \left(\frac{D_p}{2a}\right)^{1.26 \times D_f}$$

Difference between sphere and aggregate

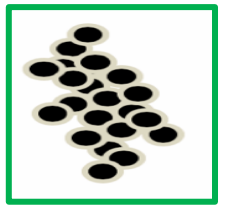
Case 1: Sphere

Radius (R) = 20 to 160 nm
Organics = 50 %

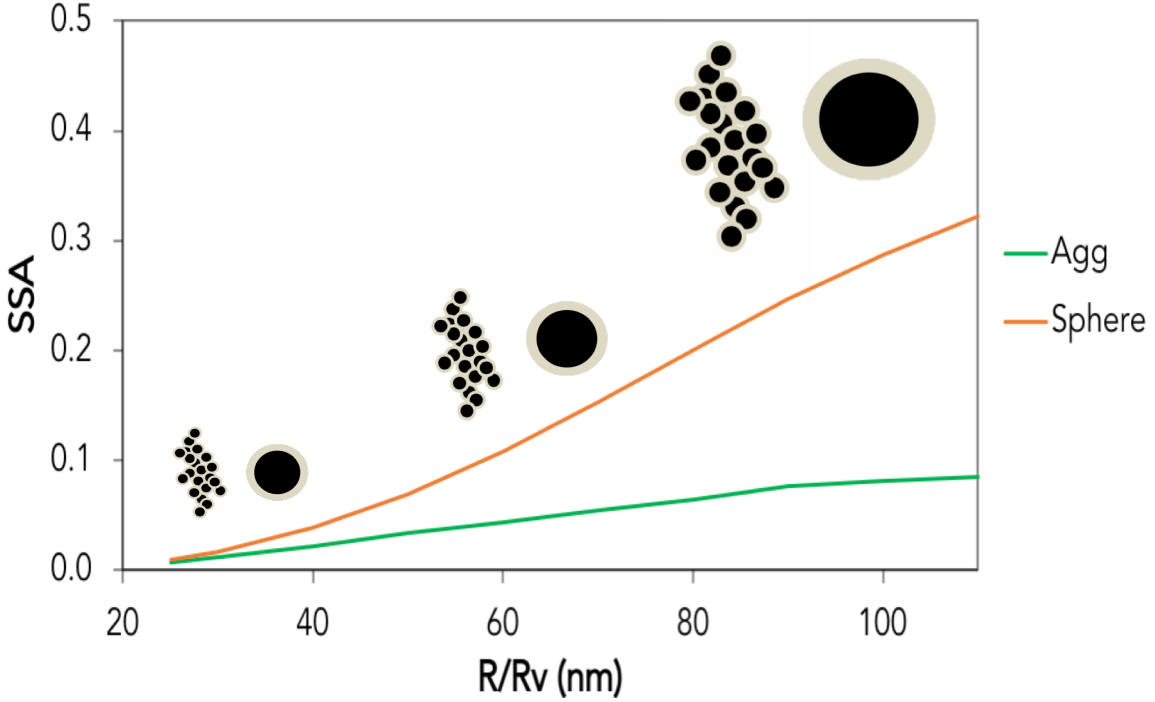


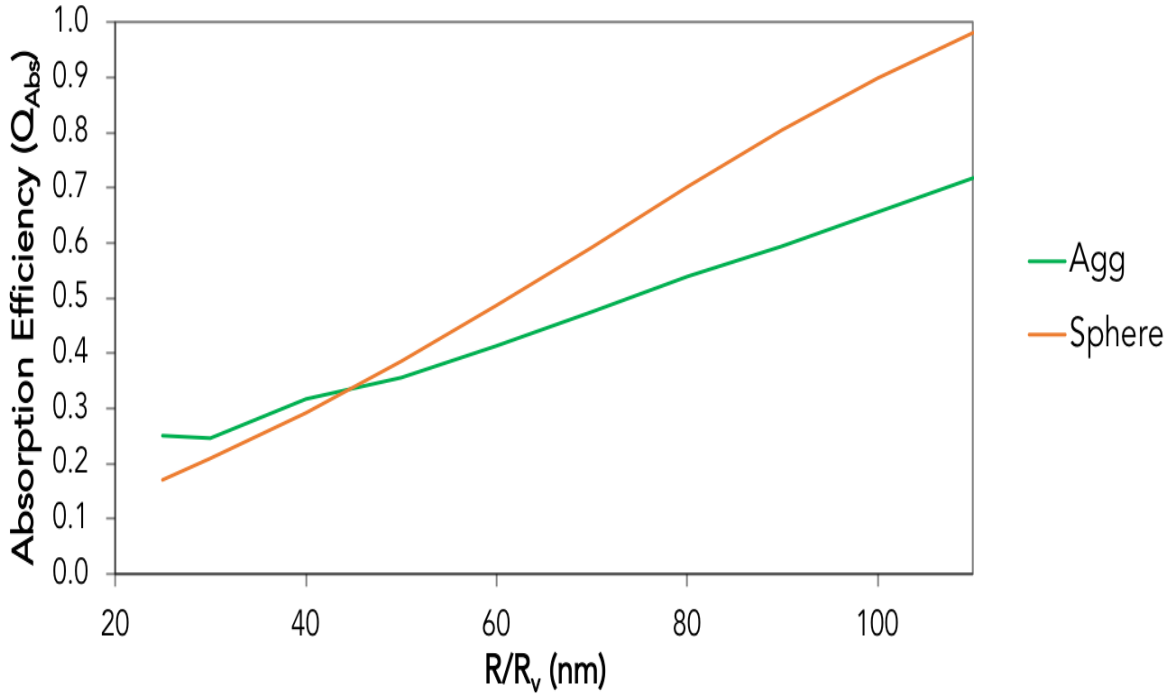
Case 2: Aggregate

Volume Equivalent Radius (R_v) = 20 to 160 nm
Organics = 50 %
Radius of primary particle (a) = 15 nm
Fractal Dimension = 1.7



Over estimation by spheres





Overview of prev. modeling studies

For BC without organics

Study	Size of Primary Particle (a)	Ns	Validation & inputs from lab
M. Kahnert	25 nm	600	None
Smith	25nm	1000	None

- Particles from combustion generators have sizes ~ 15 nm (*Ouf et al, 2016*).
- Developed parametrizations of BC for GCMs

For BC with organics

- We found Ns upto 800 in our laboratory campaign.

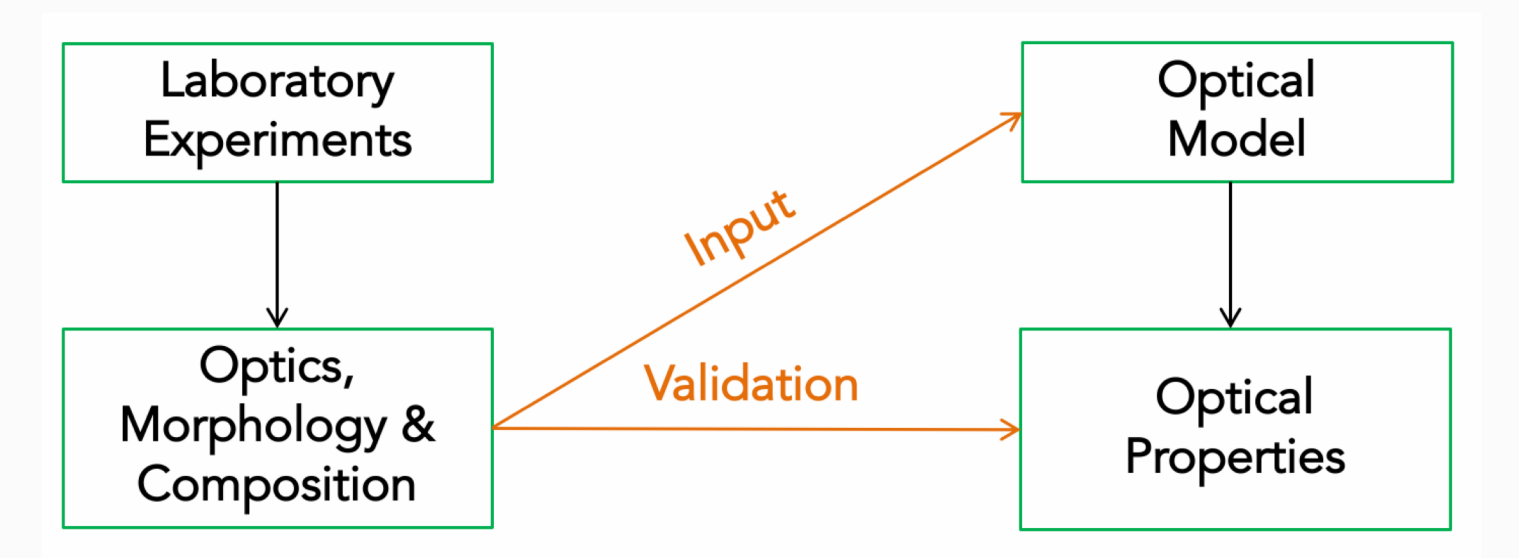
Study	Size of Primary Particle (a)	Ns	Coating method	Validation & inputs from lab
Liu	15nm	200	Single Sphere	None
Wu	25nm	300	Individual Thin	None

- Lack validation from experimental measurements.

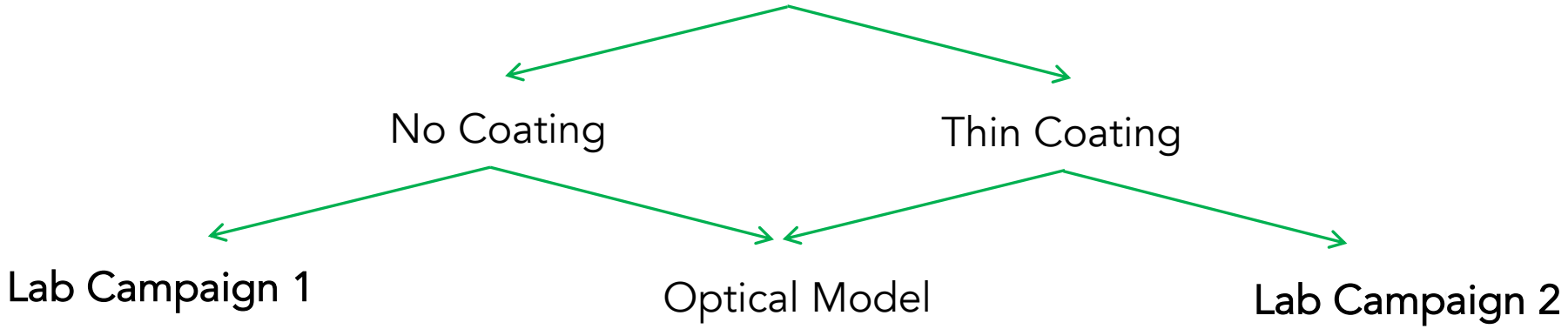
1 . Parallel experimental and modeling studies → Validation.

2. Parametrisations for thinly coated aggregates.

My Research Topic : Experimental and Modeling of Optical Properties of BC with Organics



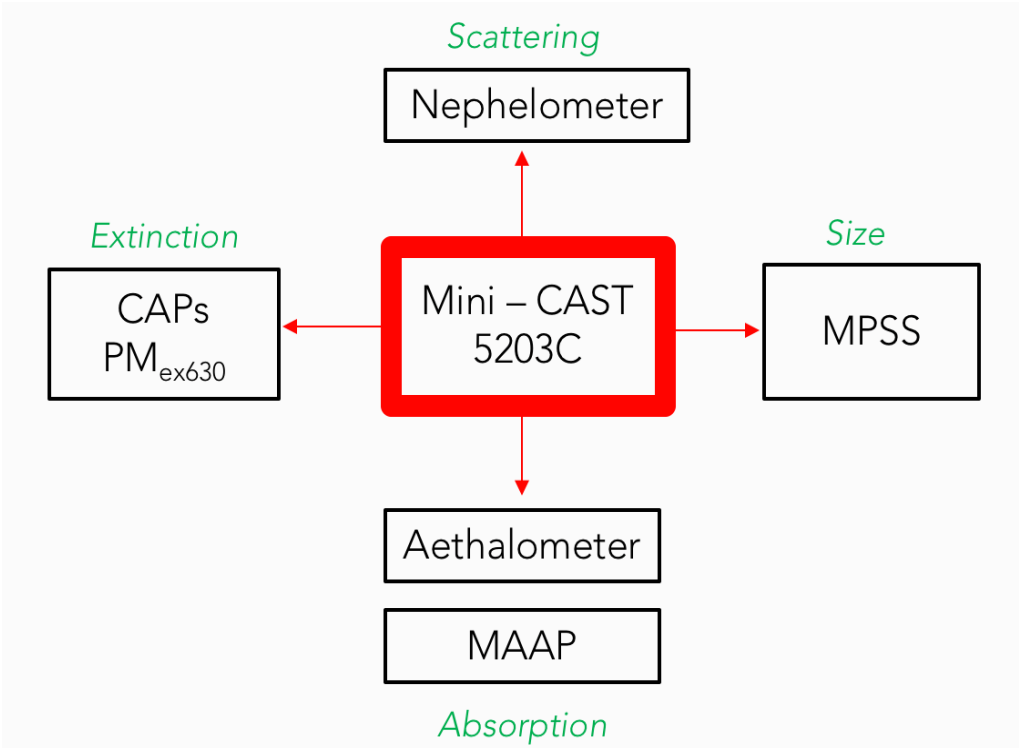
Objective 1 : Change in optical properties of black carbon with thin coating of organics.



Laboratory Campaigns – EMPIR BC Project

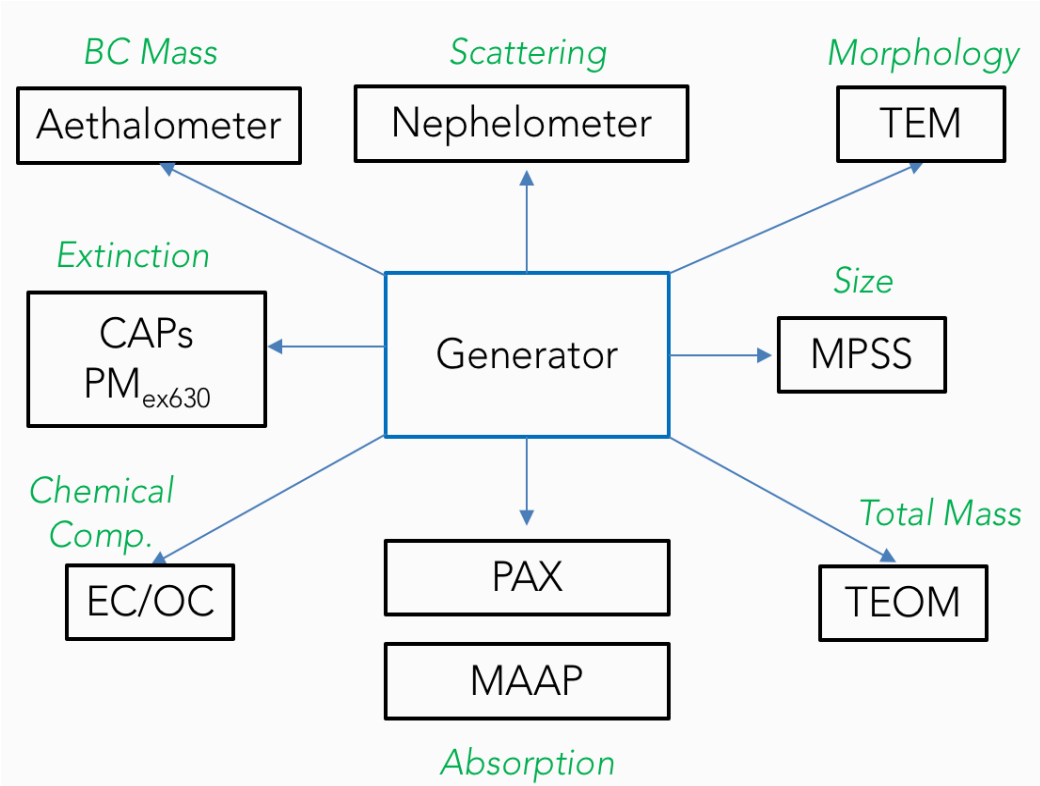
Campaign 1

- Single generator
- Pure BC (denuded)

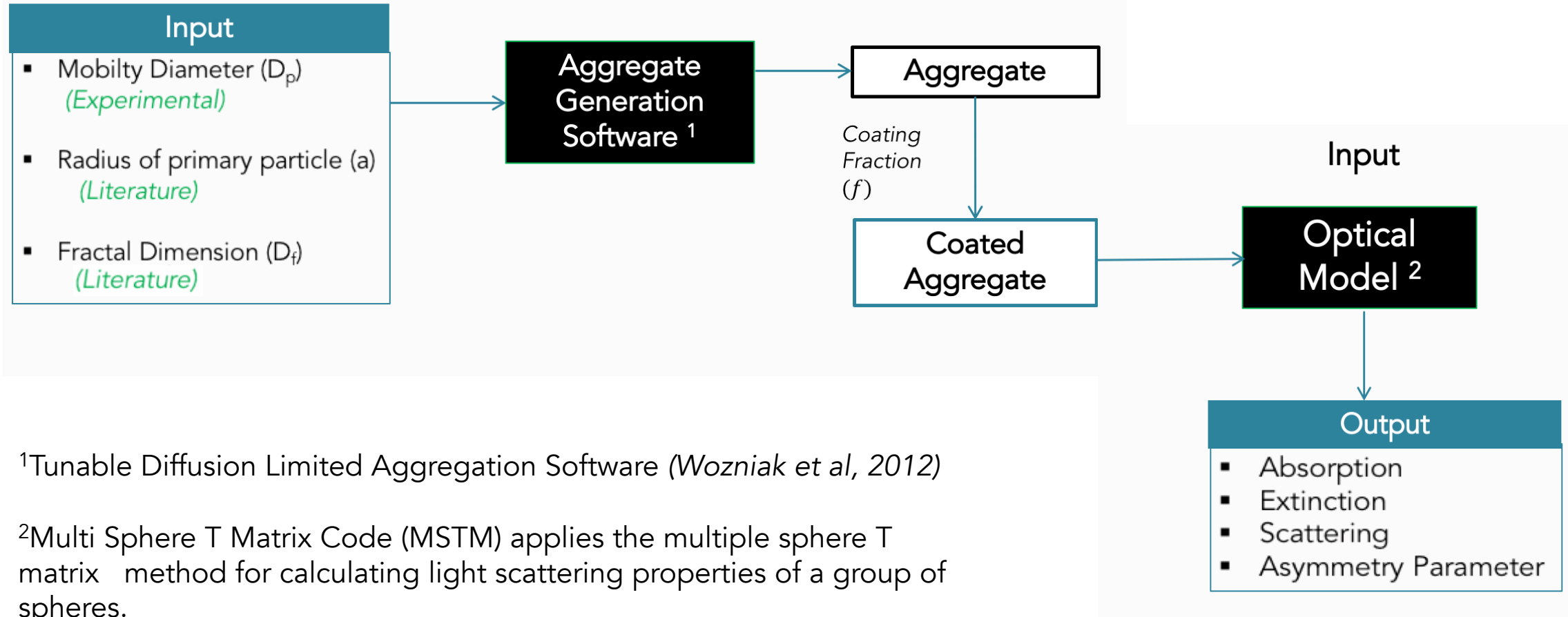


Campaign 2

- Nine generators
- BC with organics



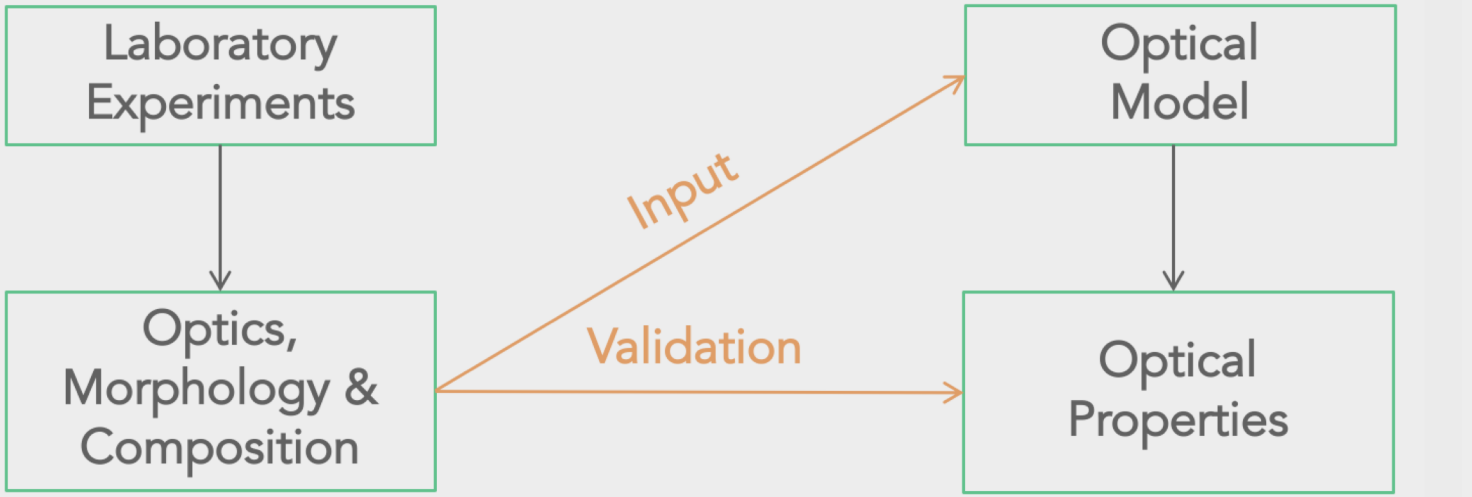
Methodology for Modeling



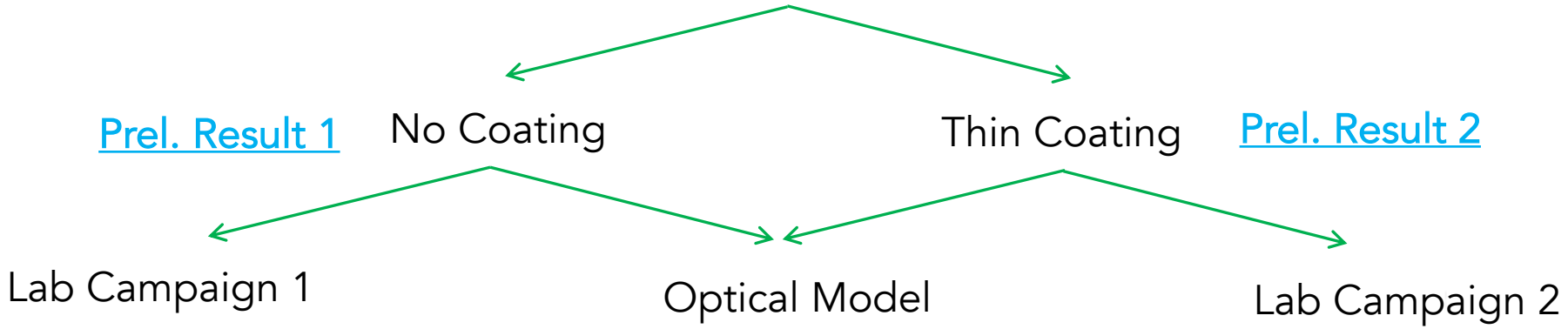
[1]Tunable Diffusion Limited Aggregation Software *(Wozniak et al, 2012)*

[2]Multi Sphere T Matrix Code (MSTM) applies the multiple sphere T matrix method for calculating light scattering properties of a group of spheres.

My Research Topic : Experimental and Modeling of Optical Properties of BC with Organics



Objective 1 : Change in optical properties of black carbon with thin coating of organics.

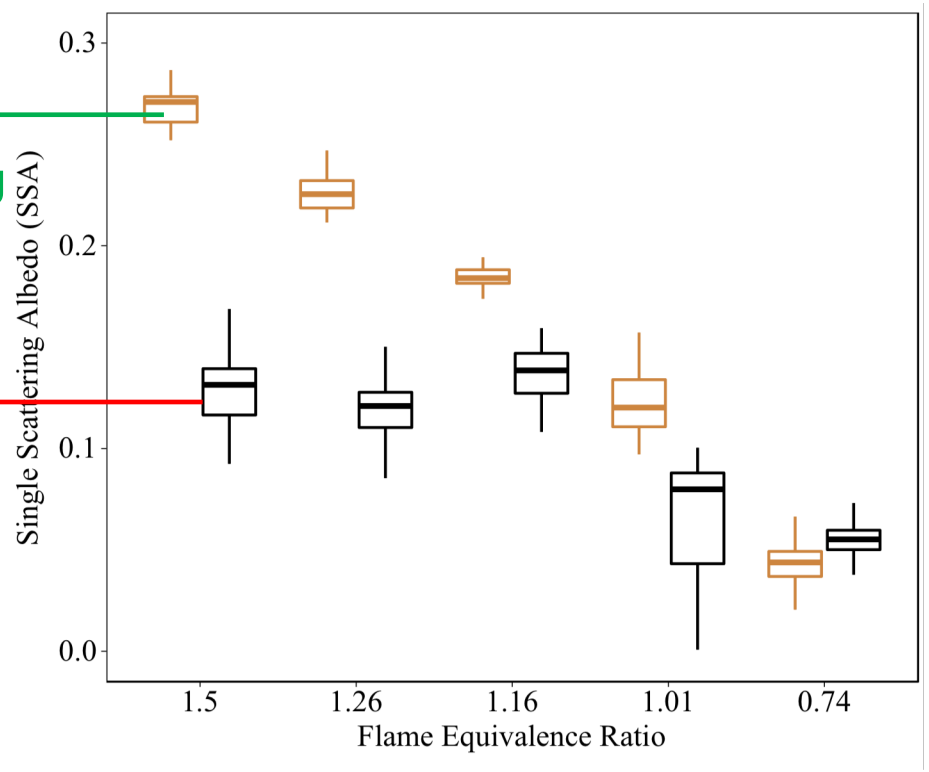


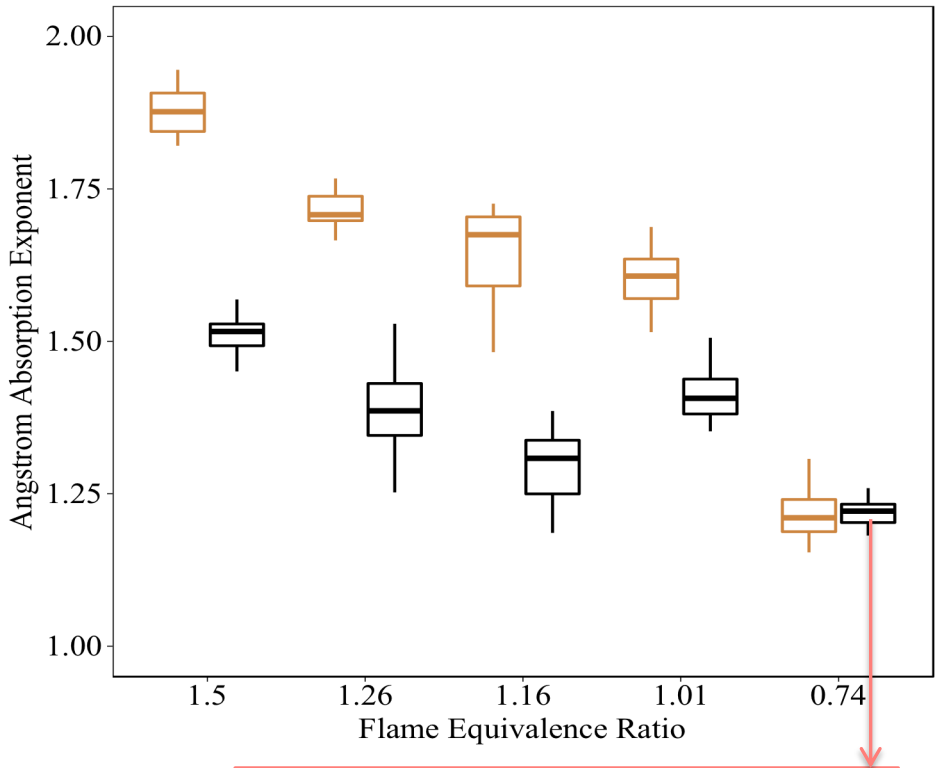
Prel. Result 1. Results from Campaign 1

- From the first campaign, the **SSA at different flame equivalence ratios**[1] (ϕ) :

Larger ϕ
Higher Scattering

After
Heating



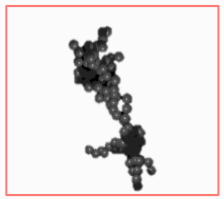
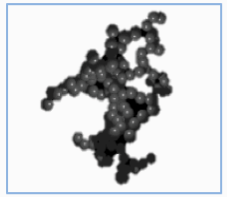
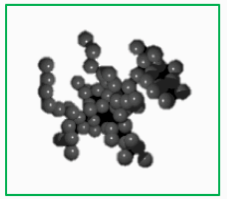


- Pure BC ⟹ Optical properties modeled
- Dependency on size, morphology and refractive index.

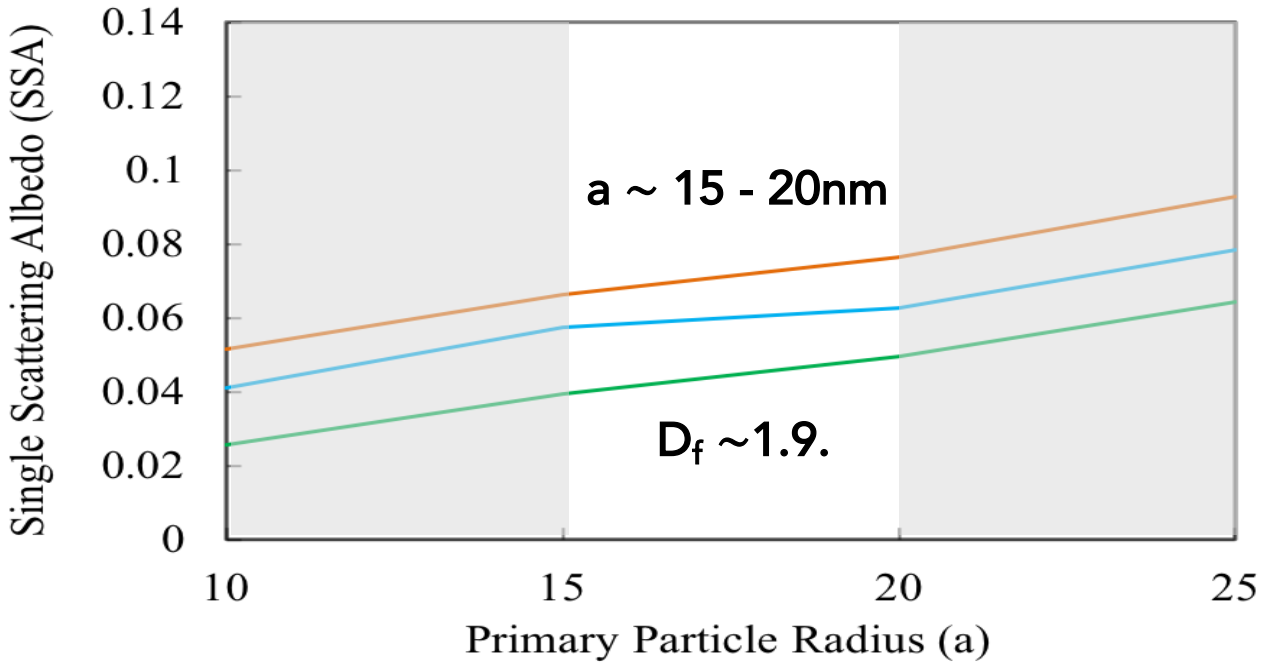
- Case with lowest organics
  Experimental SSA = 0.05
  D_p = 158nm

[1] Ratio of fuel to oxygen

Prel. Result 1. Modeled Results from Campaign 1

- D_f is expected to be 1.7 for fresh soot.
- Considering the particles : $D_f = 1.7$ →  $D_f = 1.9$ →  $D_f = 2.0$ → 
- Considering primary particle size = 10 – 25nm

Exp. SSA = 0.05



- **Results -** $SSA_{a=25} = 1.5 * SSA_{a=15}$

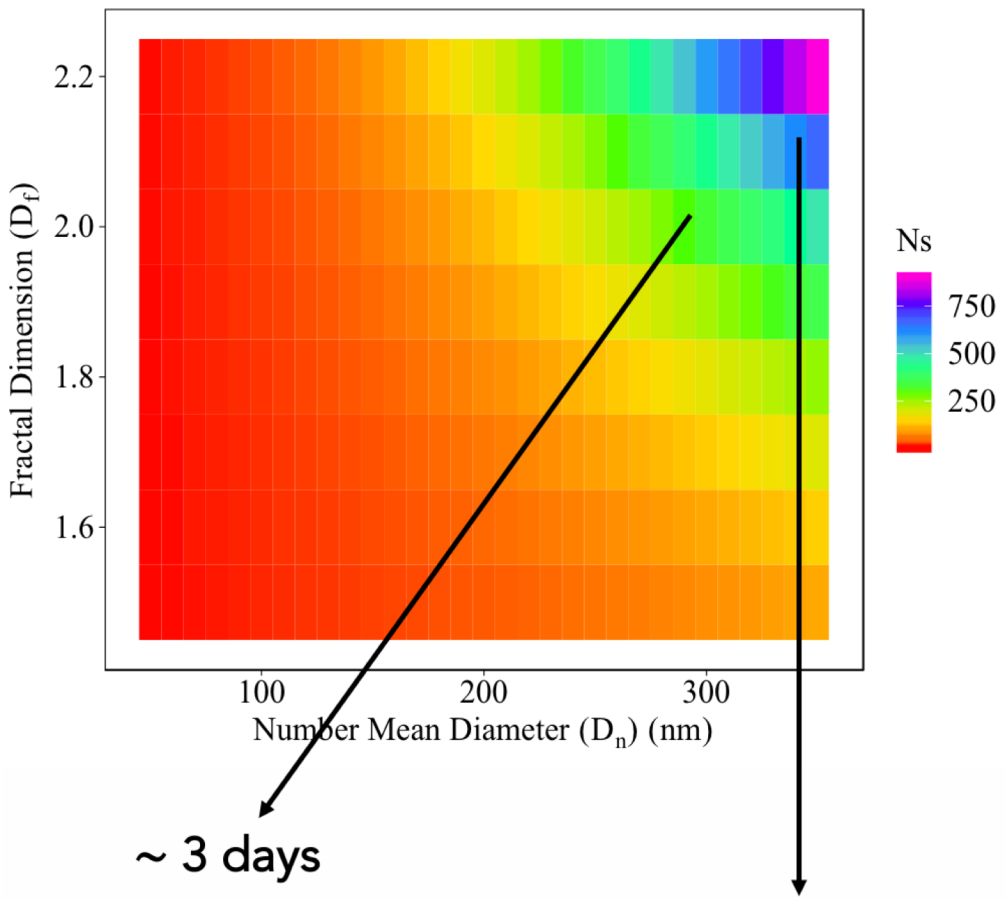
Prel. Result 2.

- In Second Campaign,
  - Number Mean Mobility Diameters (D_n) upto 300 nm.
  - For primary particle radius (a) = 15nm & D_f = 1.5 – 2.2
    - Number of primary particles (N_s) = 10 to 780.

(*Power law, Park et al, 2004*)

$$N_s = k' \left(\frac{D_n}{2a}\right)^{1.26 \times D_f}$$

  - Organics = 20% to 70% (higher than expected).
  - MSTM Code is set up to model optical properties of these aggregates with organics.



Optimizations needed For single particle ~ 280 days

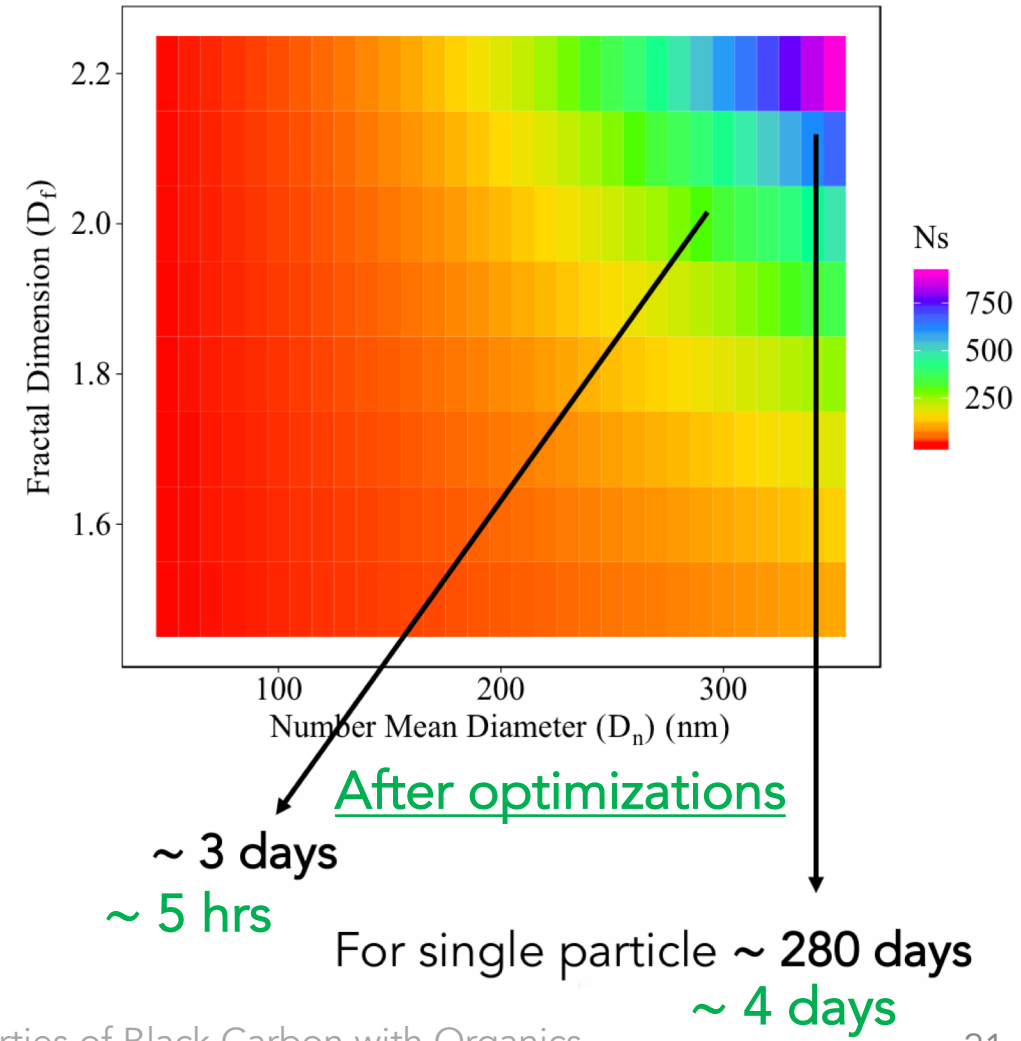
Prel. Result 2.

- In Second Campaign,
  - Number Mean Mobility Diameters (D_n) upto 300 nm.
  - For primary particle radius (a) = 15nm & D_f = 1.5 – 2.2
    - Number of primary particles (N_s) = 10 to 780.

(*Power law, Park et al, 2004*)

$$N_s = k' \left(\frac{D_n}{2a}\right)^{1.26 \times D_f}$$

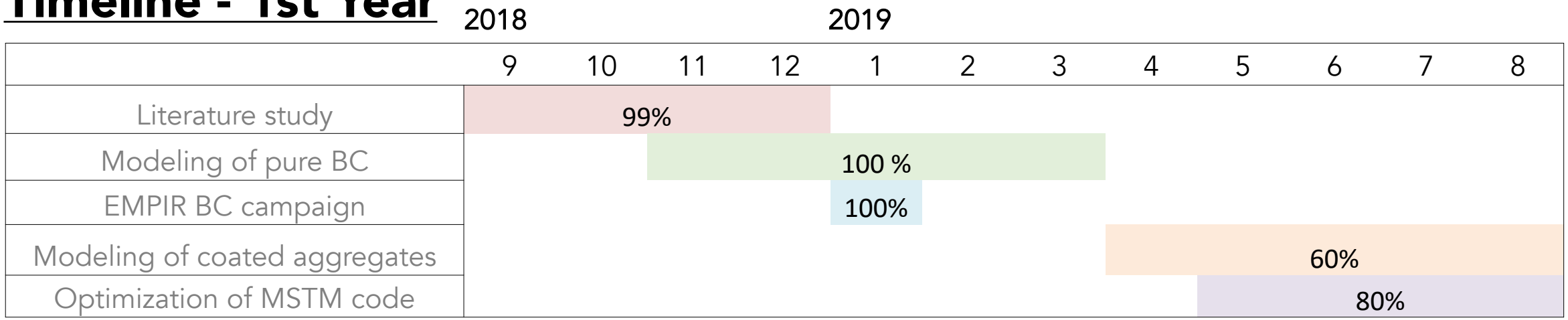
  - Organics = 20% to 80% (higher than expected).
  - MSTM Code is set up to model optical properties of these aggregates with organics.



Summary

- BC particles harm the **climate , human health and eco – system** in numerous ways.
- Organics, co-emitted with BC, **enhance the absorption of later**.
- Optical models helps in **measuring this enhancement** and **quantifying the various impacts.**
- Parallel experimental studies are required to validate the modeled optical properties.
- **My first objective :** Change in optical properties of black carbon with thin coating of organics.

Timeline - 1st Year



Outlook

- Completing the Objective 1 –
  - Result analysis and optimization of run time.
- **Objective 2** – Investigating the representation of aged BC aggregates for modeling studies.
- **Objective 3** – Parametrisations of SSA and AAE with EC/OC for BC with organics.
- **Follow up laboratory studies :**
  - Mass measurements of single particle.
  - Experiments with controlled coating.

Thank You for listening.

Special thanks, to my supervisors and group.