Capillary Condensation as an Unaccounted Pathway for Rapid Aging of Atmospheric Soot

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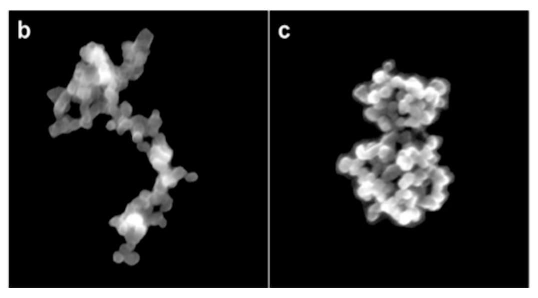
Abstract

Combustion soot is a major climate warming agent by direct forcing due to its high light absorptivity across entire solar spectrum. However, since it is initially hydrophobic, soot's indirect climate impact is insignificant at the time of emission. Fractal morphology of soot promotes rapid condensation of subsaturated vapors, such as water-soluble trace chemicals, changing its hydrophobic nature, and allowing water uptake and particle compaction at moderate humidity levels. This transformation has the potential to transform initially hydrophobic soot particles into cloud condensation nuclei (CCN).

Current atmospheric models do not account for soot's fractal morphology, instead treating particles as spheres, thus neglecting soot aging via capillary condensation.

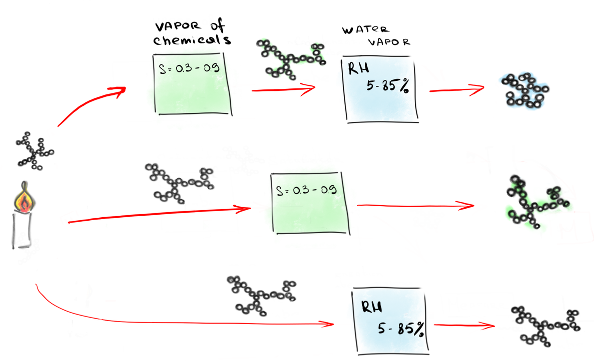


We developed a capillary condensation model for fractal soot aggregates and integrated it with the atmospheric aerosol model PartMC-MOSAIC, allowing us to evaluate the role of subsaturated trace chemicals in atmospheric soot processing. We selected an atmospheric scenario (Duke Forest, NC) corresponding to low vapor saturations, typical of atmospheric conditions dominated by biogenic emissions, and with low anthropogenic emissions of such chemicals as sulfur dioxide. PartMC-MOSAIC predicted gas composition, followed by the application of the capillary condensation model to assess condensation on fractal soot. The hygroscopic kappa theory was then used to predict the evolution of water's critical supersaturation as soot aged.

Motivation:

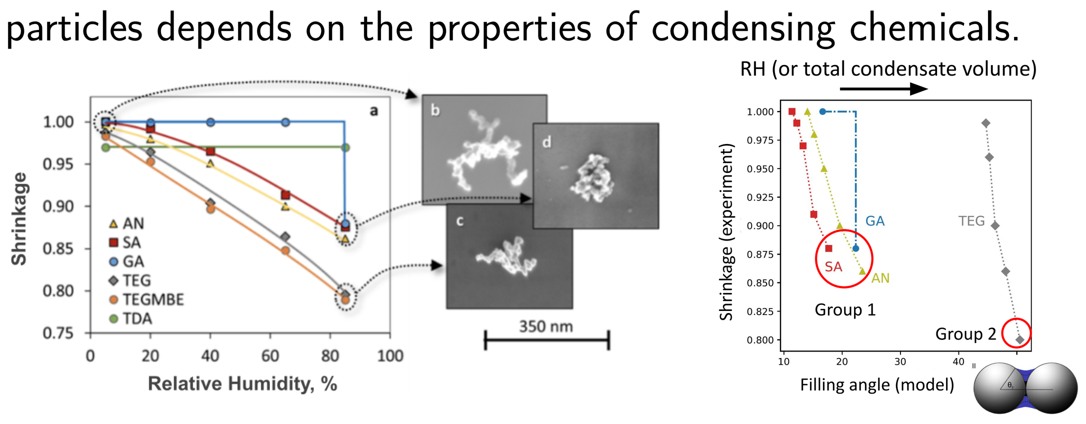
Our past experiments[1] show that capillary condensation of subsaturated vapors is possible on fractal soot due to the reduced saturation pressure above concave junctions between primary spheres. Condensate menisci induce a noticeable restructuring of fractal particles. In recent experiments, we explored the role of water-soluble condensates in the conversion of hydrophobic soot to a hydrophilic state. Soot aerosol generated in a burner was sequentially exposed to subsaturated vapor of a trace chemical and controlled humidity. The trace chemicals were ammonium nitrate, sulfuric and glutaric acids, triethylene glycol (and its monobutyl ether), and tetradecane.

- After passing soot aerosol through the first chamber to "prime" it with a chemical, minor particle shrinkage was observed, but the condensate gain was undetectable by particle mass measurement, indicating less than $2-3\%$ mass increase.



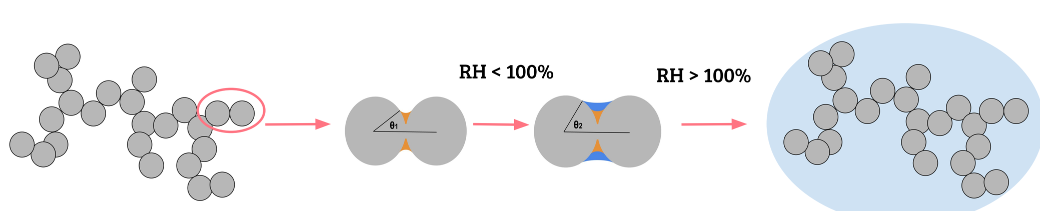
- After exposing the primed soot aerosol to controlled humidity, the particles experienced significant restructuring, which increased with increasing humidity level.

To understand experimental results, we used a capillary condensation model[1,2] to evaluate the distribution of condensed liquid on soot. The model shows that the amount of trace chemical taken by the fractal soot particles and the amount of water subsequently taken by such treated particles depends on the properties of condensing chemicals.



A larger amount of condensed water promotes more restructuring, and all chemicals can be grouped based on their restructuring ability. The model shows a good agreement with the laboratory experiments. It provides the ability to predict restructuring levels for soot aggregates depending on properties of the condensate.

However, is capillary condensation sufficient to convert hydrophobic soot into cloud condensation nuclei?

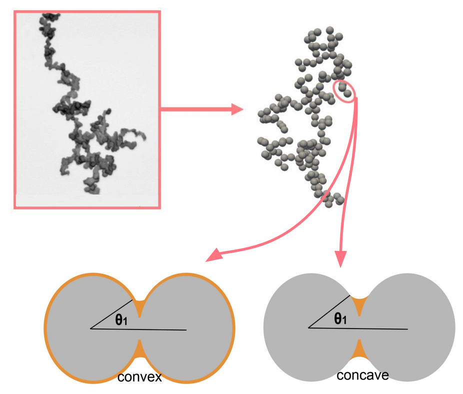


Methods:

Capillary Condensation Model

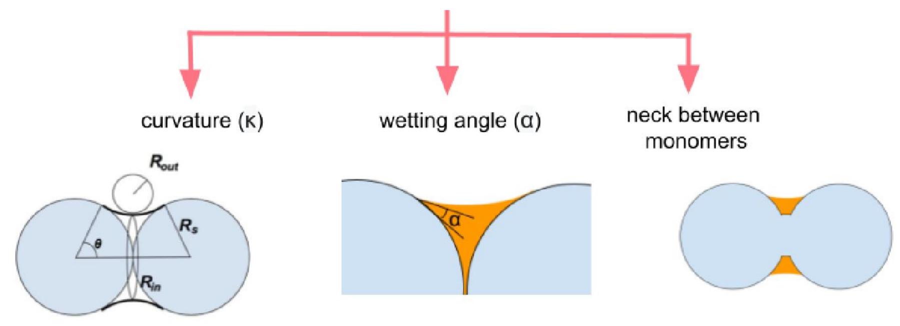
A capillary condensation model[1,2] was used to evaluate the distribution of condensed liquid on a soot aggregate. The model allowed us to estimate how quickly capillary condensation can convert hydrophobic soot to a more hydrophilic state.

- Condensation on the aggregate can be considered using two limited cases: condensation on the surface of monomers OR in the gap between monomers
- The rate of growth of a liquid shell or meniscus by vapor condensation:



$$\frac{dV}{dt} = \frac{1}{4n_l} A\alpha v_T \left(n_0 - n_\infty \exp\left[\frac{\gamma}{n_l T}\kappa\right]\right)$$

Geometry of the nano-system has a significant influence on the rate of condensation, especially due to the Kelvin effect

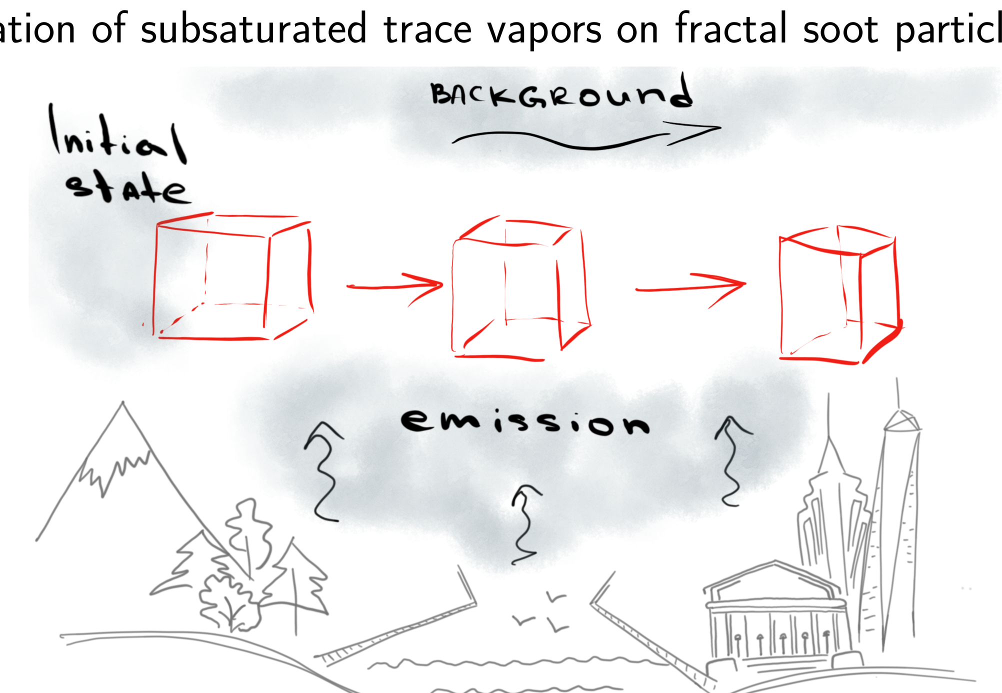


Multi Component Capillary Condensation Model

In this work, the original capillary condensation approach is extended to **multicomponent condensation** (MCCCM), where taking all components into account in the simulation enhances condensation since the partial pressure of each component decreases according to Raoult's law.

PartMC-MOSAIC

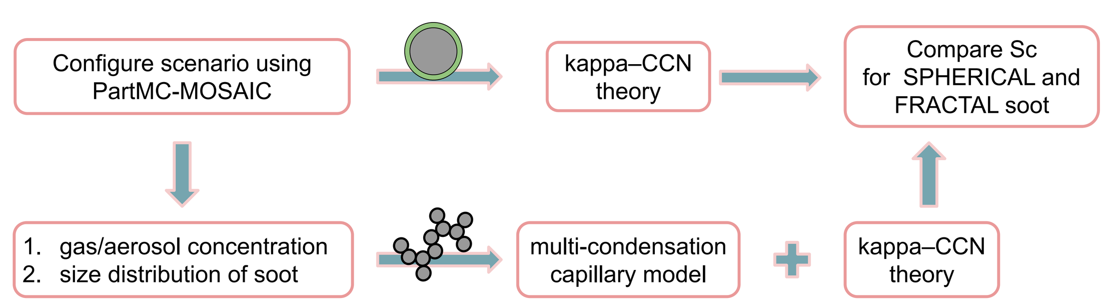
MCCCM was coupled with atmospheric aerosol model (PartMC-MOSAIC) to estimate the impact of accounting for capillary condensation of subsaturated trace vapors on fractal soot particles.



◇ PartMC = Particle-resolved Monte Carlo code for atmospheric aerosol simulation (stochastic treatments for emission, coagulation, and deposition)

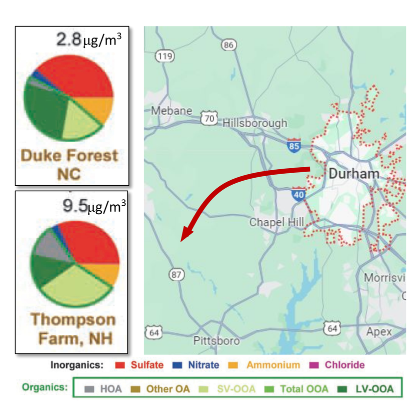
◇ MOSAIC = Model for Simulating Aerosol Interactions and Chemistry (particle phase chemistry and thermodynamics; secondary organic aerosol formation; gas-particle mass transfer)

Coupling PartMC-MOSAIC and Multi Component Capillary Condensation Model



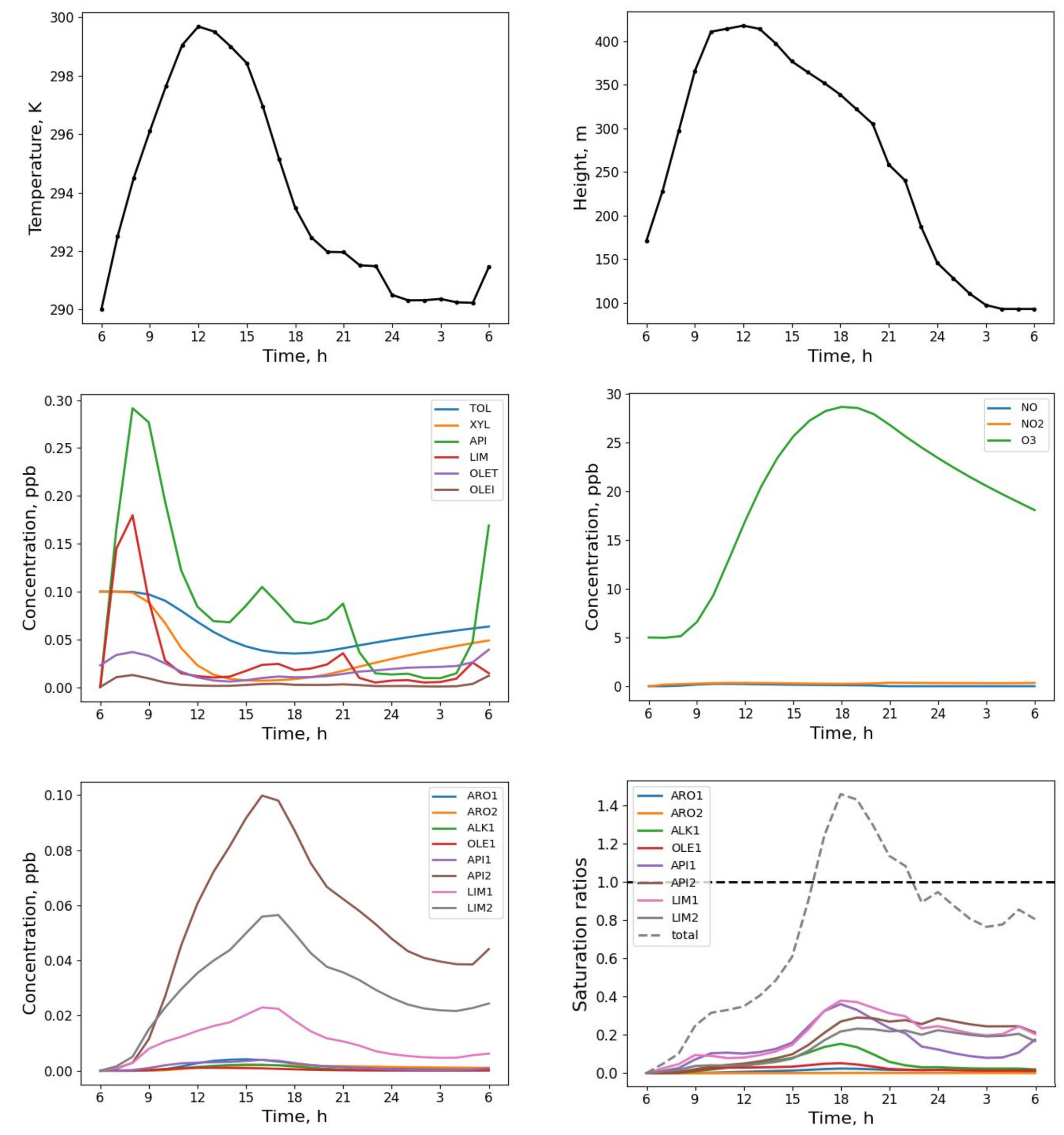
Considered scenario:

- Soot from urban emissions is transported over a forest
- Biogenic pinene and limonene are photooxidized
- Subsaturated oxidation products condense on the particles
- Hydrophobic soot gradually becomes hydrophilic

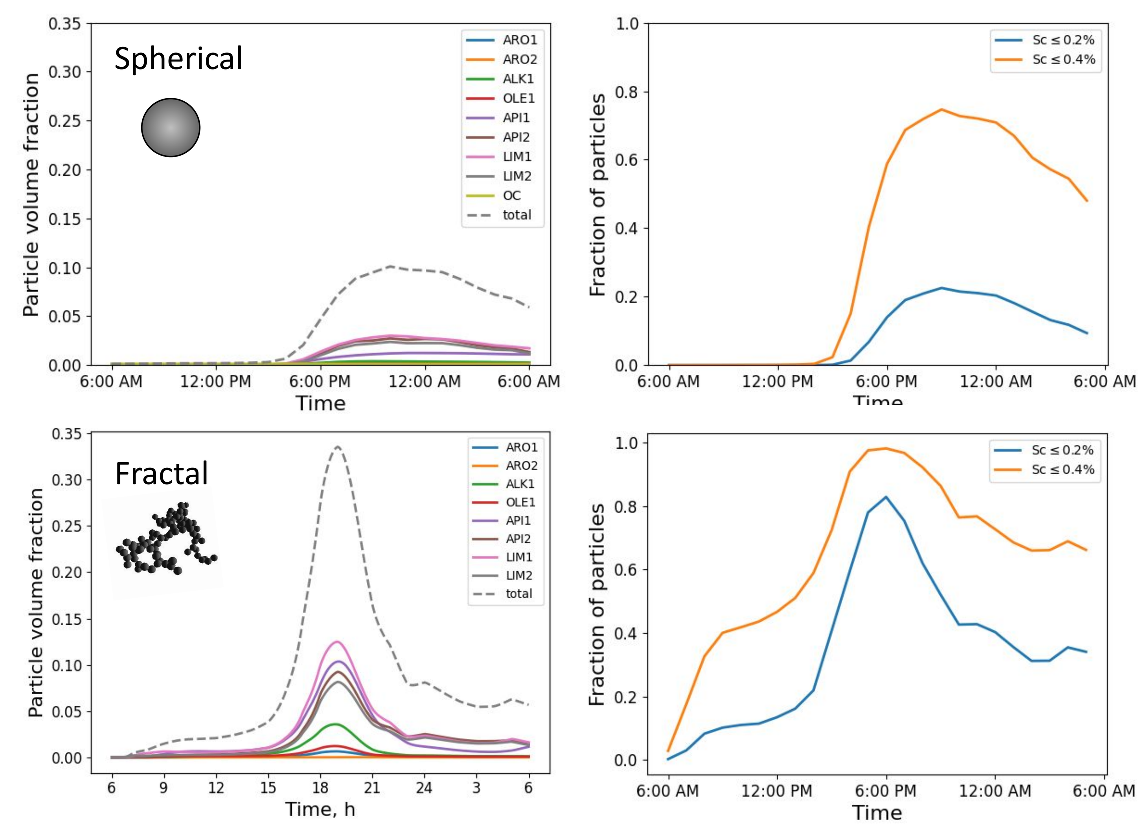


Results:

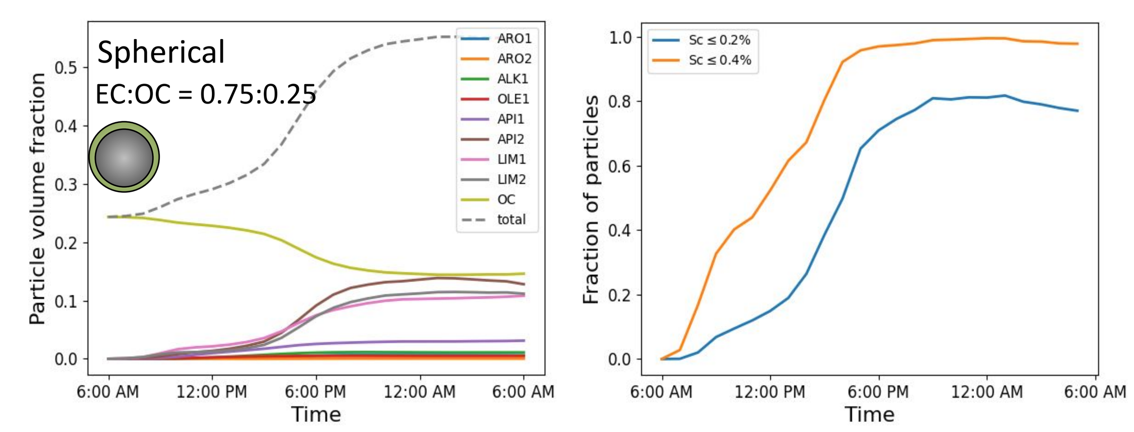
During $24\,\mathrm{h}$ gas concentration of oxidation products of antopogenic and biogenic compounds were calculated using PartMC-MOSAIC.



Comparing spherical vs fractal soot processing



Adding OC as a substitute for capillary condensation



Adding hydrophobic OC to freshly released EC (soot) increases the processing rate. However, this EC mixed with OC shows a stronger light absorption (12%) and scattering (45%).

Conclusion:

◇ In the atmosphere, subsaturated vapors can undergo capillary condensation on fractal particles, leading to soot compaction

◇ Hygroscopic condensates enhance water vapor condensation on initially hydrophobic soot, further altering particle morphology

◇ Capillary condensation of water-soluble trace chemicals alone can convert hydrophobic soot into cloud condensation nuclei

◇ Including capillary condensation in models is essential for accurate predictions of soot aging and its environmental impact

References:

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3. Ivanova, E.V., et al.; JCED 67(7), 1765, 2022
4. Khalizov, A.F., et al.; in preparation, 2024