Hygroscopicity and CCN Activity of Biomass-Burning Aerosol

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Research Overview

We measured the hygroscopic size growth factor (GF) in sub-saturated relative humidity (RH) and cloud condensation nuclei (CCN) activity in supersaturated RH of fresh biomass-burning organic carbon (OC) aerosol particles. Atmospheric processes, collectively termed 'aging', change the hygroscopic nature of OC. Our purpose is to identify reactions that affect climate-relevant properties of these ubiquitous aerosols. We compared CCN results of fresh OC with that of OC aged with reactive tracers (NH_3 and O_3) found in the lower atmosphere. RH during aging was controlled to simulate RH conditions in the lower atmosphere (5-85%), as water taken up by particles may participate in the aging reactions. We use the activation diameter (D_{50}), the diameter at which 50% of the total aerosol particles are activated, as an indicator of CCN activity. A reduction in D_{50} implies greater CCN activity. From D_{50}, we calculate the hygroscopicity parameter, κ (κ_{CCN}), and compare it with the κ obtained from GF results (κ_{GF}). Theoretically, κ_{CCN} and κ_{GF} are the same. We calculated an average $\boldsymbol{\kappa_{GF}}$ **of 0.075** for replicate tests and an average $\boldsymbol{\kappa_{CCN}}$ **of 0.077** (0.3% supersaturation). These κ values are consistent with those reported in the literature. **OC aged with 10 ppm$_v$ NH_3** for 45 min had **minimal change in D_{50}**, less than 5% reduction, for either low and high RH during aging (5% and 85%, respectively). **OC aged with high concentration of NH_3 (800 ppm$_v$) at 70% RH had a 23% decrease in D_{50}** (7% increase in potential CCN). We find **30 atmospheric-day-equivalent of NH_3 aging not affecting OC aging. Aging with 100 and 300 ppb$_v$ O_3** for 5 min (RH < 5%) showed **no change in D_{50} of the OC**, but the structure of the activation curve was different than that of fresh OC. We find that **activation behavior is more consistent across the particle population after aging; D_{50} is not sole indicator of CCN activity.**

1. Motivation

- **First indirect effect:** cloud condensation nuclei (CCN) increase the number of cloud droplets, enhance cloud albedo, cause global cooling [1].
- Pyrolysis in the anoxic core of burning biomass emits organic carbon (OC).
- CCN activity of OC depends on its hygroscopicity (represented by single-parameter, κ)[2]. κ depends on chemical composition and size.
- Atmospheric aging (coagulation, condensation, chemical reaction) alters κ of OC.
- κ and CCN activity of known-component aerosol reported often. CCN activity of OC reported less. CCN activity of aged OC not yet reported.
- We address two questions in this study:
- ➢ *What are the hygroscopic properties of actual biomass-burning OC?*
- ➢ *How does CCN Activity of the OC change upon chemical aging?*

2. Methods

1. OC Generation: Pyrolysis of oak wood at 300 °C [Fig. 1].

2. Measuring CCN Activity:

- Select dry mobility diameter and measure its η_{CCN} (s=0.3%) [Eq. 1].
- Calculate activation diameter (D_{50}) (diameter for which η_{CCN} = 50%).

3. Measuring κ (κ_{CCN} and κ_{GF}):

- κ_{CCN} – Calculate from D_{50} [Fig. 5, 6] of CCN results via Eq. 2, 3.
- κ_{GF} – Calculate from hygro. size growth factors (GF) [Fig. 4] [Eq. 4, 5].

$$\eta_{CCN} = \frac{\text{Activated Droplets (cm}^{-3})}{\text{Condensation Nuclei (cm}^{-3})} \times 100 \quad (1)$$

$$\kappa_{CCN} = \frac{4A^3}{27 D_{50}^3 \ln^2 s} \quad (2)$$

$$A = \frac{4\sigma_{s/a} M_W}{R T \rho_W} \quad (3)$$

$$\text{GF} = 1 + \left[\frac{a_w \cdot \kappa_{GF}}{1 - a_w}\right] \quad (4)$$

$$a_w = \frac{D_{RH}^3 - D_{dry}^3}{D_{RH}^3 - D_{dry}^3 \cdot (1 - \kappa_{GF})} \quad (5)$$

s = supersaturation
η_{CCN} = CCN efficiency
$\sigma_{s/a}$ = water surface tension
R = universal gas constant
a_w = water activity
T = absolute temperature
ρ_W = density of water
M_W = molar mass of water
D_{RH} = wet diameter
D_{dry} = dry diameter

3. Experimental Setup

Note: Figures 1, 2 and 3 are NOT to scale

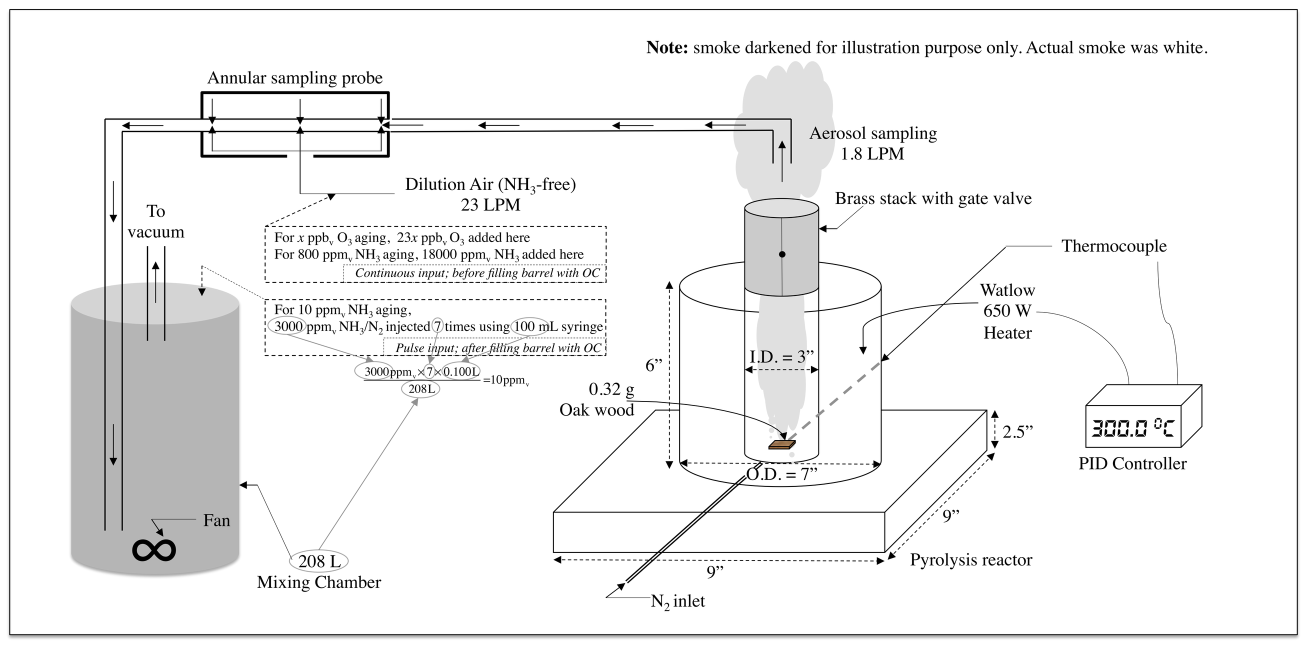

Fig. 1: OC Generation, Sampling and Handling
Aging time with NH_3 = **45 min**. Aging time with O_3 = **5 min.**
Temperature of pyrolysis = **300 °C**

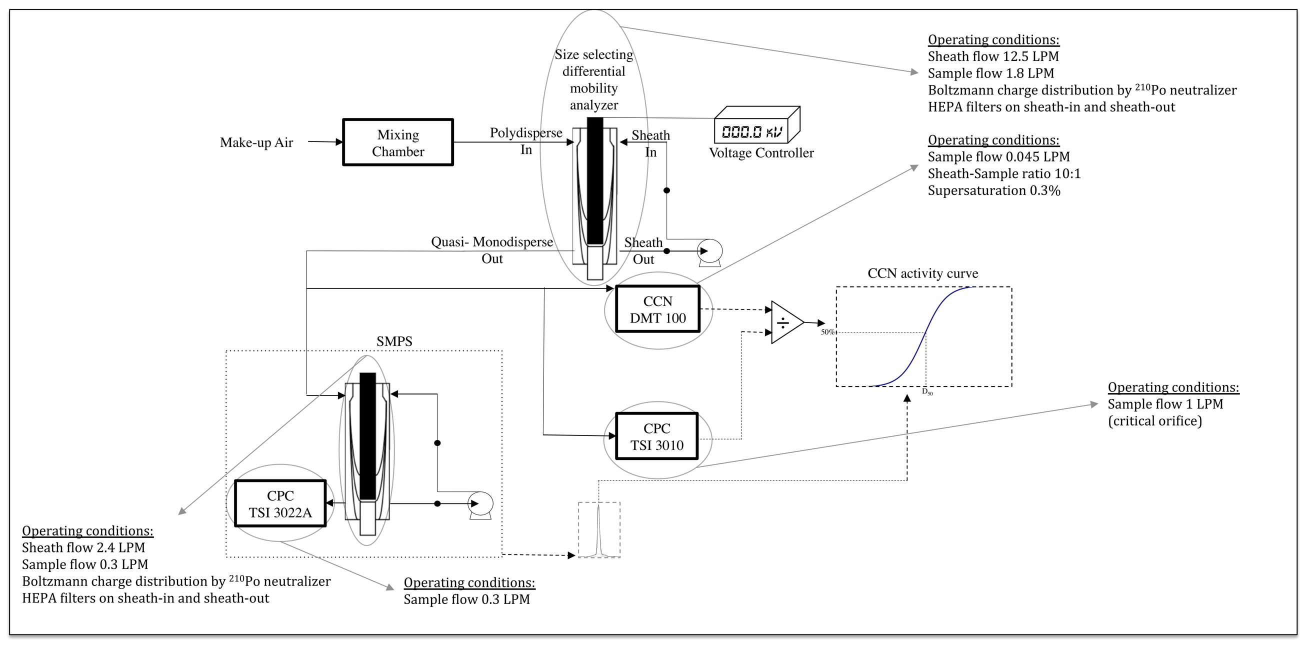

Fig. 2: CCN Measurement Setup

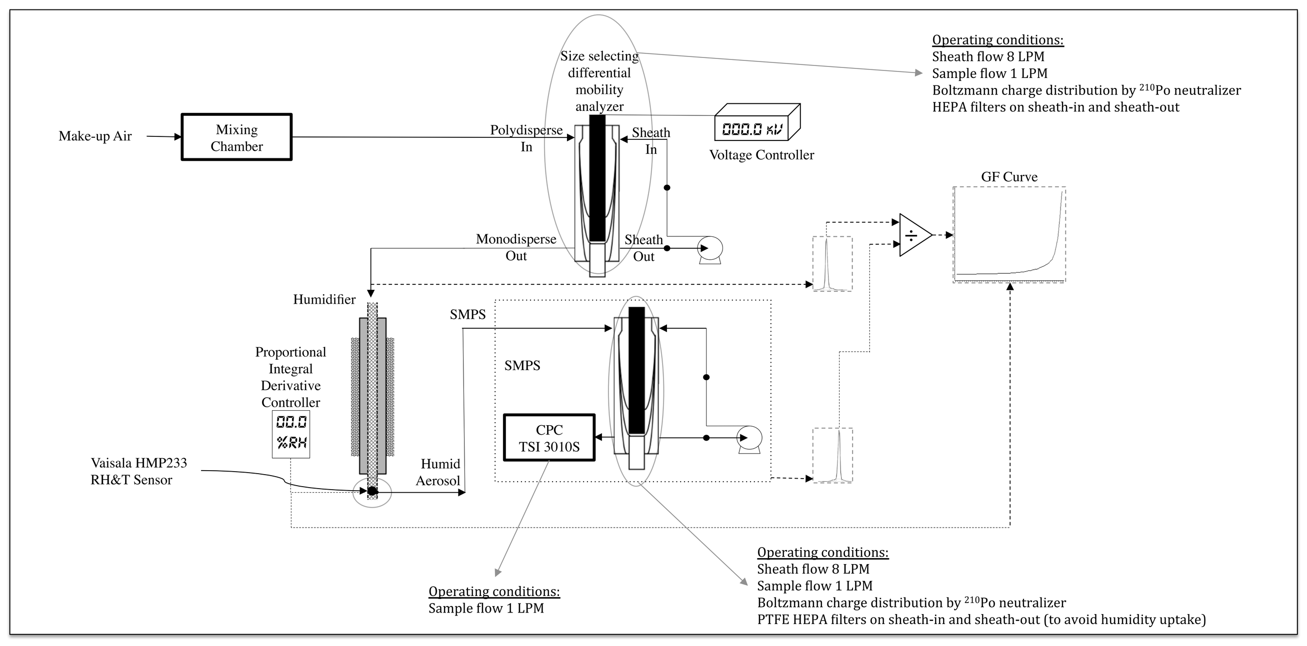

Fig. 3: GF Measurement Setup – Hygroscopic Tandem Differential Mobility Analyzer (H-TDMA)

4. Results and Discussion

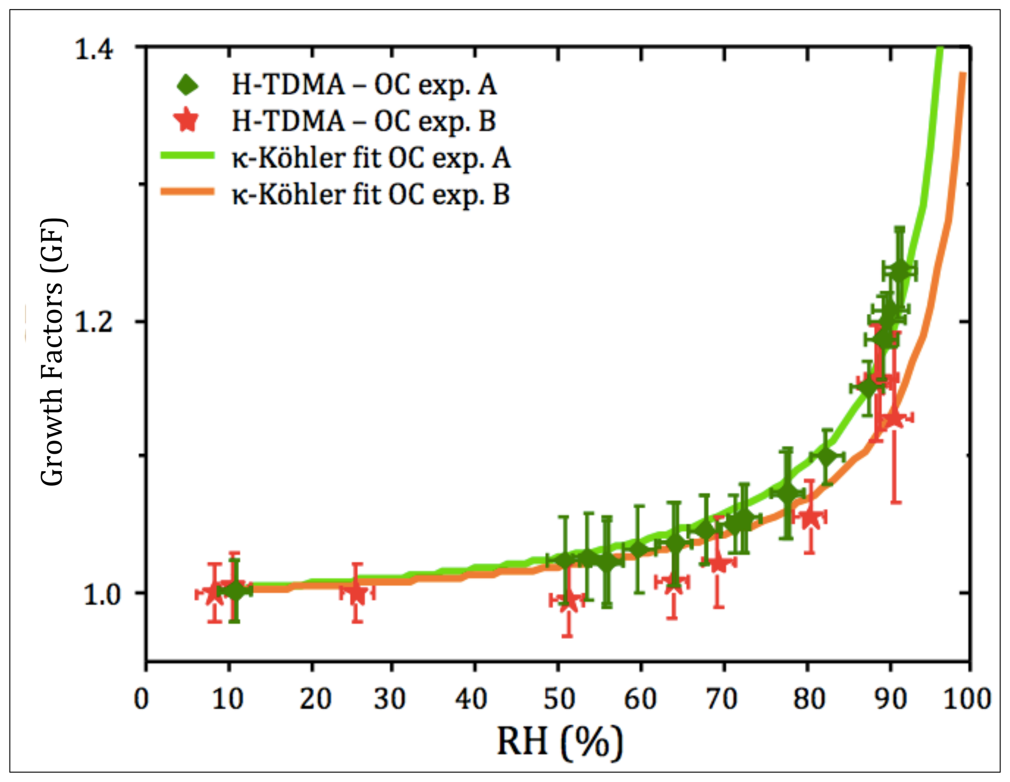

Fig. 4: Hygroscopic Size Growth Factors (GF) at controlled RH GFs analyzed using TDMAinv algorithm[3]

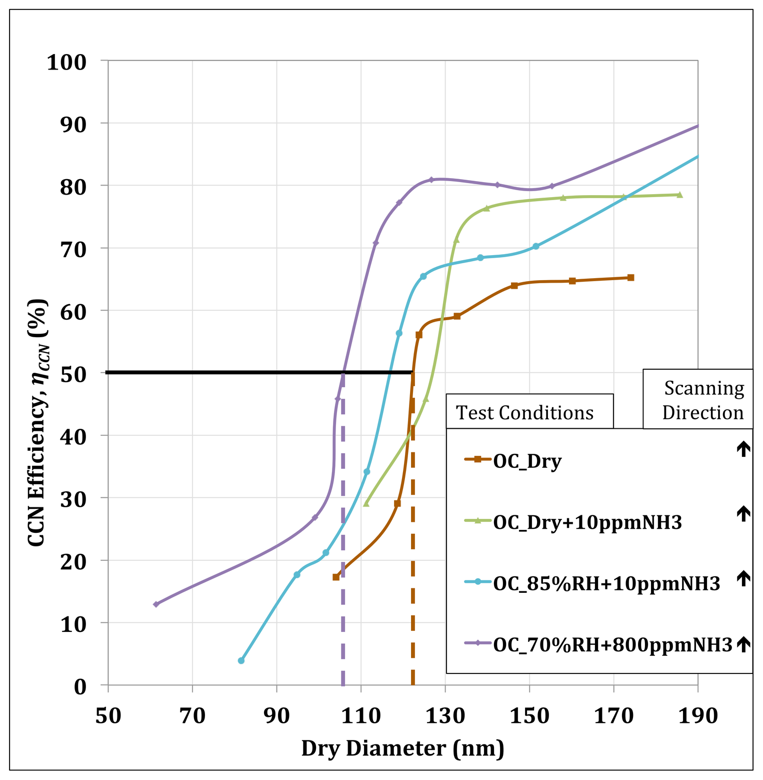

Fig. 5: CCN Activity results with Ammonia Aging

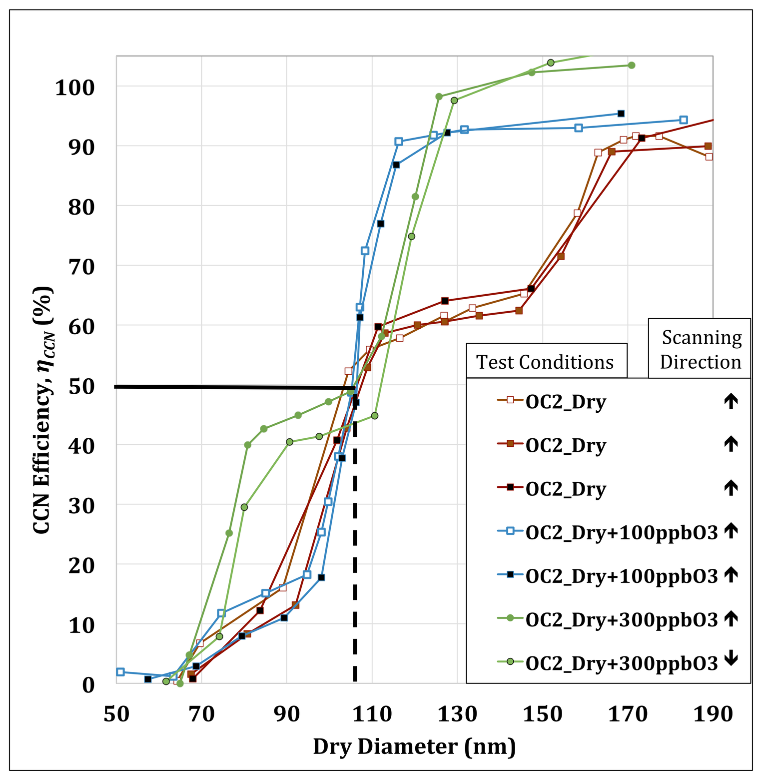

Fig. 6: CCN Activity results with Ozone Aging

Using Eq. 4, 5 — Using Eq. 2, 3 — Diameter at which η_{CCN} = 50% — Diameter at which η_{CCN} = 50%

KEY FINDINGS

κ_{GF} = 0.075 κ_{CCN} = 0.077

- κ consistent with previously reported values for high organic fraction carb. aerosol

Results with NH_3

- D_{50} = 122.7 nm for fresh OC
- Max ΔD_{50} = - 23% at 800 ppm$_v$ NH_3
- 300 atmospheric-day-equivalent of NH_3 aging not affecting aging of OC [assuming 1 ppb$_v$ atmos. NH_3 level]

Results with O_3

- D_{50} = 105.5 nm (Using Eq. 2, 3) κ_{CCN} = 0.132
- Minimal ΔD_{50} upon aging with 100 and 300 ppb$_v$ O_3
- ↑ η_{CCN} across all particles with ↑ [O_3]
- κ (and D_{50}) not sole indicator of CCNA

➢ ***What are the hygroscopic properties of actual biomass-burning OC aerosol?***

- Calculated κ values (0.075 and 0.077) **consistent with κ** reported by Engelhart et al.[4] **for OC with high organic fraction** (> 80% by mass).
- The value of κ (and D_{50}) for fresh OC different in Fig. 5 than Fig. 6: source of biomass was different. Engelhart et al.[4] reported a convergence of κ (and D_{50}) after 3-5 hours of photochemical aging for aerosols from burning of different biomass species.

➢ ***How does the CCN activity of actual biomass-burning aerosol change upon aging?***

- Largest change in CCN activity (23% ΔD_{50}) seen for 800 ppm$_v$ NH_3 aging [Fig. 5]. Based on particle size distribution, this corresponds to 7% increase in CCN. **We find 300 atmospheric-day-equivalent of NH_3 aging does not participate in aging mechanisms of OC** [assuming 1 ppb$_v$ atmos. NH_3 level].
- $\boldsymbol{D_{50}}$ **of OC does not change upon aging with 100 and 300 ppb$_v$ O_3** [Fig. 6]. Scan direction was reversed at 300 ppb$_v$ O_3 aging to see effects of exposure time. No changes observed [Fig. 6].
- **Structure of the CCN activity curve changes** and a more **consistent increase in $\boldsymbol{\eta_{CCN}}$** observed across the size distribution with increasing [O_3]. We find that **κ (and D_{50}) is not a sole indicator of CCN activity** and the activity curve cannot be reconstructed from D_{50} alone. Size-resolved CCN activity should be measured to characterize aging impact on CCN activity of OC.

References.

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