The importance of aerosol composition and mixing state on predicted CCN concentration and the variation of the importance with atmospheric processing of aerosol

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1. INTRODUCTION

One of the challenges in quantifying aerosol indirect effects is to determine the spectrum of cloud condensation nuclei (CCN) and its spatial and temporal variations on global scale. At a given supersaturation, CCN concentration is determined by aerosol size distribution, chemical composition, and mixing state. Due to computational constraints, representation of aerosol properties, such as aerosol composition and mixing state, is often simplified in global models. Currently there is no consensus on the importance of detailed knowledge of aerosol composition and mixing state on the prediction of CCN concentrations. In some studies, CCN concentration is found to be well predicted using simplified composition and mixing state, whereas other studies suggests CCN concentration can only be reproduced when detailed chemical composition, mixing state, and the properties of organics are taken into consideration.

In this study, the importance of particle composition and mixing state on predicted CCN concentration and the variation of the importance with atmospheric processing of aerosol are examined using measurements taken at an urban (T0) supersite during Megacity Initiative: Local and Global Research Observations (MILAGRO).

2. MEASUREMENTS

Data were collected during MILAGRO at the T0 supersite, which is located at the Instituto Mexicano del Petroleo (IMP), 9 km NNE of the center of Mexico City, near a combination of residential, commercial and light industrial areas. Aerosol measurements presented in this study were taken from the top of a building (Building 32, Fig. 1), ~28 m above ground level, from 10 to 31 March 2006.

Figure 1. T0 supersite site at Instituto Mexicano del Petroleo (IMP) in Mexico City.

Table 1. Aerosol measurements presented in this study.

Property measured	Size range	Instrument	Time Resolution
Aerosol size spectrum	$15<D_p<560$ nm	Scanning Mobility Particle Sizer (SMPS)	2 min
CCN conc. (S= 0.11, 0.17, 0.22, 0.29, and 0.35%)	N/A	DMT CCN counter	36 min
Size-resolved aerosol mixing state	7 sizes from 13 to 400 nm	Humidified Tandem DMA (H-TDMA)	~30 min
Size-resolved non-refractory species	$60<D_{va}<1000$ nm	Aerodyne HR-ToF-AMS	2.5 min
Black Carbon (BC) mass concentration	<2000 nm	Aethalometer	2 min

3. DIURNAL VARIAITONS OF OBSERVED AEROSOL PROPERTIES

Increased HOA (i.e., primary organic aerosol), BC, and nucleation mode particle concentrations associated with morning and evening traffic. A large fraction of particles are non-hygroscopic, suggesting freshly emitted HOA and BC are externally mixed with other species.

Increased nitrate and oxygenated OA concentrations due to photochemical production. Growth factor distribution changes from bimodal to unimodal, suggesting species become more internally mixed as secondary species condense on pre-existing particles.

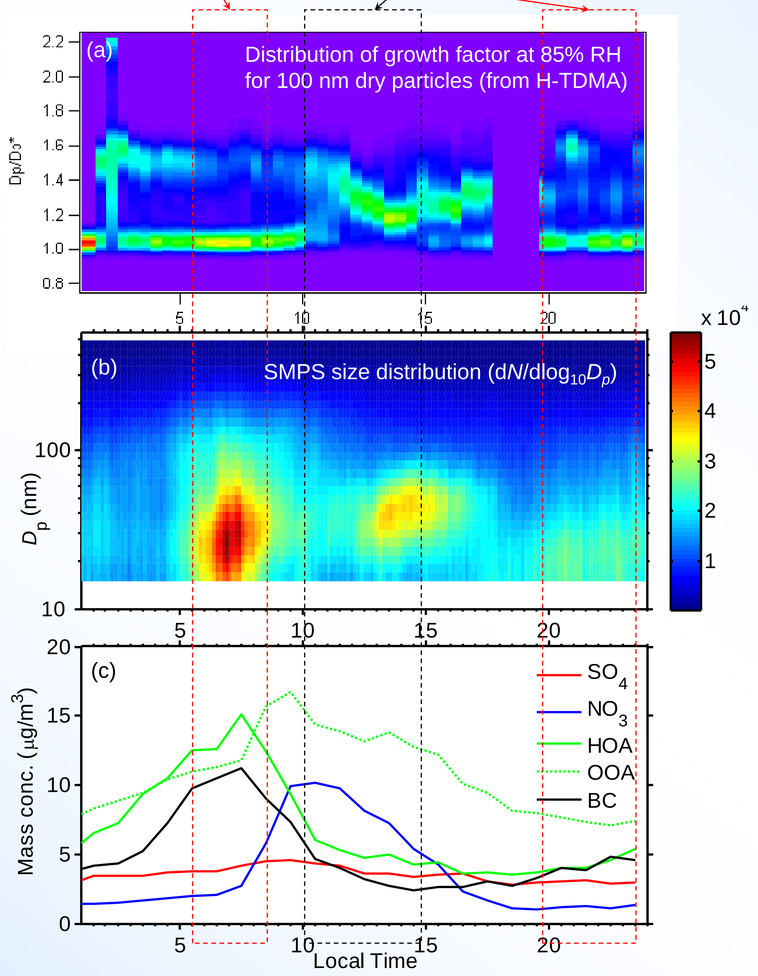


Figure 2. Diurnal variations of aerosol properties observed at the T0 site during weekdays. (a) Distribution of growth factor at 85% RH for 100 nm dry particles. (b) Aerosol size distribution measured by SMPS. (c) Mass concentrations of SO_4, NO_3, hydrocarbon-like organic aerosol (HOA), oxygenated organic aerosol (OOA, consisting mainly of secondary organic aerosol and biomass burning organic aerosol), and black carbon (BC).

4. EFFECT OF AEROSOL COMPOSOSTION AND MIXING STATE ON PREDICTED CCN CONCENTRATION.

CCN concentrations are calculated using four different assumptions of aerosol chemical composition and mixing state, and are compared to concurrent measurements at the T0 site. The four assumptions are:

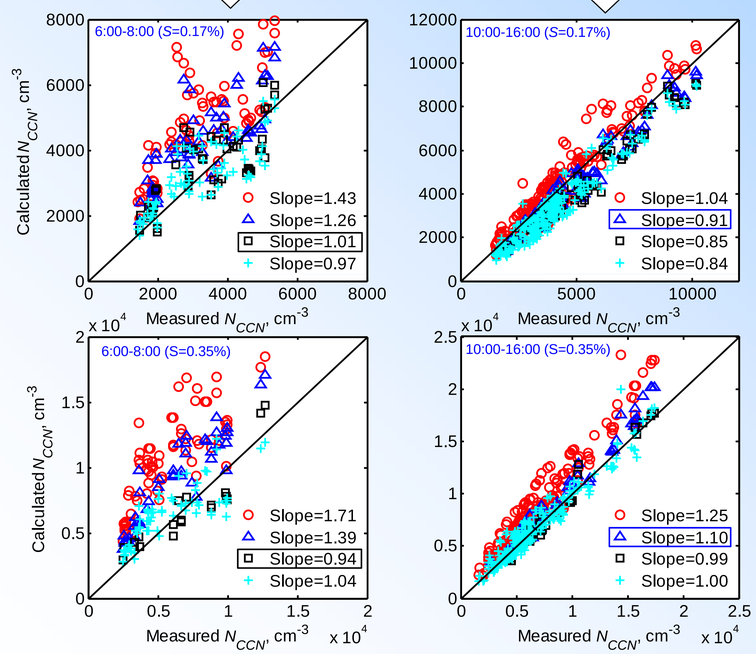
- ***Assumption 1: internal mixture with constant composition (i.e., average composition derived from bulk measurements).***
- ***Assumption 2: internal mixture with size-resolved composition.***
- ***Assumption 3: Sulfate, nitrate, and OOA internally mixed, BC and HOA externally mixed, size-resolved composition.***
- ***Assumption 4: external mixture with constant (i.e. bulk) composition.***

Table 2. Species hygroscopicity used to calculate CCN concentration.

Species	$(NH_4)_2SO_4$	NH_4NO_3	HOA	OOA	BC
Hygroscopicity (κ)	0.61	0.74	0 (insoluble)	0.15	0 (insoluble)

Large differences among CCN concentrations calculated using different assumptions. The strong impact of aerosol mixing state and composition on calculated CCN concentration is due to the high volume fraction (52%) of non-hygroscopic HOA and BC during 6:00-8:00.

Photochemical production of hygroscopic species (nitrate and SOA) rapidly reduces the contribution of HOA and BC (23% by volume), and therefore the influence of assumed mixing state on calculated CCN concentrations during 10:00-16:00.



- Assumption 1: Internal mixture, constant (i.e. bulk) composition.
- Assumption 2: Internal mixture, size-resolved composition.
- Assumption 3: HOA and BC ext. mixed, size-resolved composition
- Assumption 4: External mixture, constant (i.e. bulk) composition.

Figure 3. Comparison of CCN concentrations calculated using four different assumptions and the measurements at 0.17% and 0.35% supersaturations for the periods of 6:00-8:00 and 10:00-16:00. The fitted slope corresponding to the most appropriate assumption is highlighted..

5. CONCLUSIONS

- During daytime, freshly emitted primary organic aerosols (POA) and black carbon (BC) are rapidly coated (in ~3 hours) by nitrate and SOA produced through photochemical reactions. As a result, CCN concentrations are well predicted by assuming internally mixed aerosols, and using bulk compositions. This suggests that urban aerosols may be treated as internal mixtures once they are a few tens of kilometers away from their sources.

- Assumed aerosol mixing state strongly impacts predicted CCN concentration only when non-hygroscopic species (i.e., POA and BC) represent a large fraction of total aerosol volume. One of the implications is that while physically unrealistic, external mixtures, which are often used in global models, may also sufficiently predict CCN concentrations for aged aerosols, because the contribution of non-hygroscopic POA and BC to the overall volume of aged aerosols is often substantially reduced due to the condensation of secondary hygroscopic species.

6. ACKNOWLEDGEMENTS

- Atmospheric System Research, US Department of Energy for funding support.
- Mexican Institute of Petroleum for hosting the T0 supersite.
- Logistics support from Molina Center for Energy and the Environment, Mexican government agencies and institutions.