New-particle formation and growth at the DOE Southern Great Plains field site in Oklahoma

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Processes shaping aerosol size distribution

- Nucleation
- Coagulation
- Condensation/uptake
- Cloud processing / aqueous chemistry
- Deposition
- Primary Emissions

Particle Number

~1 nm

Ultrafine (Aitken) mode

Accumulation mode
- Cloud Condensation Nuclei (CCN)
- Aerosol scattering/absorption

Particle Size

>1 μm

Primary Emissions
Deposition
Primary Emissions
Deposition
Nucleation/growth contribute climate relevant particles

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- Accumulation mode
  - Cloud Condensation Nuclei (CCN)
  - Aerosol scattering/absorption

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~1 nm

Nucleation

Coagulation

Condensation/uptake

Cloud processing / aqueous chemistry

>1 μm

Particle Size

Primary Emissions

Deposition

Primary Emissions

Deposition
Early growth processes less studied than nucleation

- Ultrafine (Aitken) mode
- Accumulation mode
  - Cloud Condensation Nuclei (CCN)
  - Aerosol scattering/absorption

Particle Number

~1 nm

Primary Emissions

Deposition

Condensation/uptake

Cloud processing / aqueous chemistry

>1 μm

Particle Size

Primary Emissions

Deposition
Recent work (e.g. Westervelt et al., 2013) shows that details of growth more important than nucleation rates for climate properties.

Condensing/uptake material must be (or become) very low volatility.

Early growth processes less studied than nucleation.
Potential pathways of low-volatility material for growth

Gas-phase chem w/ condensation
Reversible condensation/evaporation
(or ~irreversible condensation for low vapor pressures)

Accretion (oligomerization) reactions:
X and/or Y are organic, react to form low volatility species (Z)
* may be related to high-viscosity particles?

Acid-base chemistry:
A and/or B are organic
Potential pathways of low-volatility material for growth

Gas-phase chem w/ condensation
Reversible condensation/evaporation
(or ~irreversible condensation for low vapor pressures)

Accretion (oligomerization) reactions:
X and/or Y are organic, react to form low volatility species (Z)
* may be related to high-viscosity particles?

• Only “Gas-phase chem w/ condensation” explicitly included in 3D aerosol models.
• Models may fudge condensation to “correct” for lack of other processes to get growth rates right on average.
• Will lack day-to-day variations chemical details.
Potential pathways of low-volatility material for growth

Gas-phase chem w/ condensation
Reversible condensation/evaporation
(or ~irreversible condensation for low vapor pressures)

Accretion (oligomerization) reactions:
X and/or Y are organic, react to form low volatility species (Z)
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- Only “Gas-phase chem w/ condensation” explicitly included in 3D aerosol models.
- Models may fudge condensation to “correct” for lack of other processes to get growth rates right on average.
  - Will lack day-to-day variations chemical details.
- NEED PROCESS-BASED UNDERSTANDING FOR MODELS
DOE DE-SC0011780: Contributions of organic compounds to the growth of freshly nucleated atmospheric nanoparticles

• Goals
  • Analysis of formation/growth during DOE ASR: “Southern Great Plains – New Particle Formation Study (NPFS)"
  • Controlled laboratory studies of growth mechanisms
  • Parameterize growth for aerosol models
  • Test in regional/global aerosol models
DOE DE-SC0011780: Contributions of organic compounds to the growth of freshly nucleated atmospheric nanoparticles

**Goals**

- Analysis of formation/growth during DOE ASR: “Southern Great Plains – New Particle Formation Study (NPFS)”
- Controlled laboratory studies of growth mechanisms
- Parameterize growth for aerosol models
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Current focus (in first year of work)
DOE DE-SC0011780: Contributions of organic compounds to the growth of freshly nucleated atmospheric nanoparticles

• Goals

  This talk

  • Analysis of formation/growth during DOE ASR: “Southern Great Plains – New Particle Formation Study (NPFS)”

  • Controlled laboratory studies of growth mechanisms

  • Parameterize growth for aerosol models

  • Test in regional/global aerosol models
SGP New Particle Formation Study (NPFS)

- April - May 2013: 18 observed NPF events
- Measurements in addition to core ARM observations (UMN, Augsburg, NCAR, UDEL)
  - Nanoparticle composition (TDCIMS and NAMS)
  - Particle size distribution: 1.5 nm to 1 μm (SMPS + DEG-CPC)
  - Size-resolved nanoparticle volatility and hygroscopicity (UV/UHTDMA)
  - Aerosol gas-phase precursors (ammonia, amines, sulfuric acid; CIMS)
  - Vertically resolved aerosol number concentrations (dual-CPCs on tethered balloon)
A tale of 3 growth events
A tale of 3 growth events

From size distributions alone, events look qualitatively similar in many ways.

Only with the combinations of instruments available during SGP-NPFS we learn that growth on each day was through a different pathway.
May 11, 2013: Growth by sulfuric-acid/amines/organics

Gas-phase acids

Gas-phase bases

Size distribution (points show size of composition measurement)
May 11, 2013: Growth by sulfuric-acid/amines/organics

Gas-phase acids

Gas-phase bases

Ultrafine particle composition

Size distribution (points show size of composition measurement)

Hour of Day

Pos. Mean Dp
Neg. Mean Dp

H2SO4 + H2SO4 dimer
oxalic acid
malonic acid
ammonia
methyl amine+DMA+TMA
C4-C7 amine sum
Ammon.
Amine/Amide
Org. w/ S
Org. w/ N
Org.
Sulfate
Nitrate (org/inorg)
Org. w/ N
Org.
May 11, 2015: Growth by sulfuric-acid/amines/organics

Gas-phase acids

Gas-phase bases

Ultrafine particle composition

Size distribution (points show size of composition measurement)

Moderate sulfuric acid
May 11, 2013: Growth by sulfuric-acid/amines/organics

- **Gas-phase acids**
- **Gas-phase bases**
- **Ultrafine particle composition**
- **Size distribution** (points show size of composition measurement)

**Chart Details**
- **Large-amine concs. similar to ammonia**
- **Moderate sulfuric acid**
- **H2SO4 + H2SO4 dimer**
- **Oxalic acid**
- **Malonic acid**

**Legend**
- Ammonia
- Methyl amine+DMA+TMA
- C4-C7 amine sum
- Ammon.
- Amine/Amide
- Org. w/ S
- Org. w/ N
- Org.
- Sulfate
- Nitrate (org/inorg)
- Org. w/ N
- Org.
- Pos. Mean Dp
- Neg. Mean Dp

**Y-axis**
- Gas-phase acids: cm$^{-3}$
- Gas-phase bases: pptv
- Positive Ion Signal: 0 to 0.8
- Negative Ion Signal: 0 to 0.8
- Size distribution: $10^2$ to $10^1$ nm

**X-axis**
- Hour of Day
May 11, 2013: Growth by sulfuric-acid/amines/organics

Gas-phase acids

Gas-phase bases

Ultrafine particle composition

Size distribution (points show size of composition measurement)

Moderate sulfuric acid

Large-amine concs. similar to ammonia

Sulfuric acid, amines and organics all important

Pos. Mean Dp
Neg. Mean Dp

Hour of Day
May 11, 2013: Growth by sulfuric-acid/amines/organics

Flow from North:
No major urban areas
Agriculture
April 19, 2013: Growth by organics

**Gas-phase acids**

**Gas-phase bases**

**Ultrafine particle composition**

**Size distribution** (points show size of composition measurement)
April 19, 2013: Growth by organics

Gas-phase acids

Gas-phase bases

Ultrafine particle composition

Size distribution (points show size of composition measurement)

Low sulfuric acid

H2SO4 + H2SO4 dimer
malonic acid

ammonia
methyl amine+DMA+TMA
C4-C7 amine sum

Amine/Amide
Org. w/ N
Org.
Nitrate (org/inorg)
Org. w/ N

Pos. Mean Dp
Neg. Mean Dp

Hour of Day
April 19, 2013: Growth by organics

Gas-phase acids

Gas-phase bases

Ultrafine particle composition

Size distribution (points show size of composition measurement)

Low sulfuric acid

Large-amine concs. similar to ammonia

Amine/Amide

Org. w/ N

Org.

Nitrate (org/inorg)

Org. w/ N

Pos. Mean Dp

Neg. Mean Dp
April 19, 2013: Growth by organics

Gas-phase acids

Gas-phase bases

Ultrafine particle composition

Size distribution (points show size of composition measurement)

Large-amine concs. similar to ammonia

Low sulfuric acid

Only organics and amines
April 19, 2013: Growth by organics

Flow from North:
No major urban areas
Agriculture
May 9, 2013: Growth by sulfuric-acid/ammonia

Gas-phase acids

Gas-phase bases

Ultrafine particle composition

Size distribution (points show size of composition measurement)

Hour of Day

5.9.13

H2SO4 + H2SO4 dimer
oxalic acid
malonic acid
ammonia
methyl amine+DMA+TMA
C4-C7 amine sum
Ammon.
Amine/Amide
Org. w/ S
Org. w/ N
Org.

Sulfate
Nitrate (org/inorg)
Org. w/ N
Org.

Pos. Mean Dp
Neg. Mean Dp
May 9, 2013: Growth by sulfuric-acid/ammonia

Gas-phase acids

Gas-phase bases

Ultrafine particle composition

Size distribution (points show size of composition measurement)

Very high sulfuric acid
May 9, 2013: Growth by sulfuric-acid/ammonia

Gas-phase acids

Gas-phase bases

Ultrafine particle composition

Size distribution (points show size of composition measurement)

Very high sulfuric acid

Amines somewhat lower than other days
May 9, 2013: Growth by sulfuric-acid/ammonia

Gas-phase acids

Gas-phase bases

Ultrafine particle composition

Size distribution (points show size of composition measurement)

Very high sulfuric acid

Amines somewhat lower than other days

Ammonium sulfate with some organics and amines

Ultrafine particle composition

Gas-phase acids

Gas-phase bases

Ultrafine particle composition

Size distribution (points show size of composition measurement)
May 9, 2013: Growth by sulfuric-acid/ammonia

NOAA HYSPLIT MODEL
Backward trajectories ending at 1700 UTC 09 May 13
NAM Meteorological Data

Flow from South:
Major urban areas (e.g. Dallas)
Industrial gulf coast
NPFS-2013: vertical profiles of 10-20 nm diameter aerosol

No nucleation at surface at start of flight

Surface size distribution

Balloon-borne nucleation-mode aerosol
No nucleation at surface at start of flight

Nucleation aloft during ascent

Balloon-borne nucleation-mode aerosol
NPFS-2013: vertical profiles of 10-20 nm diameter aerosol

No nucleation at surface at start of flight

Nucleation aloft during ascent

Particles mixed to surface by end of descent
Nucleation aloft!

Implication: yesterday's residual layer important
Does dry deposition in surface layer overnight remove precursors?

Captured in GEOS-Chem-TOMAS regional modeling results (below)

No nucleation start of flight
Nucleation aloft
Particles mixed end of descent

[Graph showing total particle number vertical profile]
Take home points

- DOE-funded New Particle Formation Study at ARM SGP site
  - Unprecedented collection instruments for NPF/growth/precursor measurements
  - At least 3 distinct pathways for new-particle growth observed
  - Various pathways not resolved in models
  - Nucleation observed to start aloft
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- Next steps with field study
  - Do gas-phase species and particle growth fit our understanding of thermodynamics and kinetics?
  - Explore all field-study days... patterns?
Take home points

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  - Unprecedented collection instruments for NPF/growth/precursor measurements
  - At least 3 distinct pathways for new-particle growth observed

Future goals

- Controlled lab studies of growth pathways
- Growth parameterization building
- Test against field observations

- Do gas-phase species and particle growth fit our understanding of thermodynamics and kinetics?
- Explore all field-study days... patterns?
May 11, 2013: Can track through night... similar event on May 12

Gas-phase acids

Gas-phase bases

Ultrafine particle composition

Size distribution (points show size of composition measurement)