NO\textsubscript{x} effects on atmospheric aerosol formation: Suppression? Innocent bystander? Enhancement?

Volatile Organic Compounds (VOCs) 

\[ \text{VOCs} \rightarrow \text{OH, O}_3, \text{NO}_3 \rightarrow \text{NO}_2 \rightarrow \text{oxyVOCs (incl. nitrates)} \]

Climate effects?

Juliane L. Fry
fry@reed.edu
Assistant Professor of Chemistry
Reed College, Portland, OR
NO\textsubscript{x} effects on atmospheric aerosol formation: Suppression? Innocent bystander? Enhancement?

Volatile Organic Compounds (VOCs) → OH, O\textsubscript{3}, NO\textsubscript{3} → NO\textsubscript{2} (incl. nitrates) → oxyVOCs → AIR QUALITY → CLIMATE effects?

Juliane L. Fry
fry@reed.edu
Assistant Professor of Chemistry
Reed College, Portland, OR
Atmospheric aerosol (=particles)

Figure courtesy D. Lamb, PSU
Motivation: Aerosol-climate interaction

Source: SeaWiFS satellite

Source: Terra/MODIS satellite

http://visibleearth.nasa.gov
Motivation: Aerosol-climate interaction

Source: IPCC Fourth Assessment Report, 2007
What do we need to learn to narrow uncertainties on these aerosol climate forcings?

- Aerosol formation mechanisms & kinetics
- Atmospheric lifetime (loss processes)
- Chemical composition
- Optical properties
- Cloud interactions (hydroscopicity, etc.)
Motivation: Aerosol-climate interaction

What do we need to learn to narrow uncertainties on these aerosol climate forcings?

- Aerosol formation mechanisms & kinetics
- Atmospheric lifetime (loss processes)
- Chemical composition
- Optical properties
- Cloud interactions (hydroscopicity, etc.)

Source: IPCC Fourth Assessment Report, 2007
Motivation: Focus on secondary organic aerosol (SOA)

SOA formation:

VOCs → OH, O₃, NO₃ → ...... → oxyVOCs

Later-generation oxidation steps important to SOA formation – SOA formation may occur far from VOC emission sources

Formation of secondary organic aerosol

Kanakidou et al, 2005: SOA source: 12 – 70 Tg aerosol year⁻¹
Large missing source of organic aerosol

Several field campaigns showed models dramatically underestimating SOA globally.

Volkamer et al, GRL, 2006
Large missing source of organic aerosol

Several field campaigns showed models dramatically underestimating SOA globally.

SOA source estimates:
Kanakidou et al, 2005: 12 – 70 Tg aerosol year\(^{-1}\)
Goldstein & Galbally, 2007: 140 – 910 Tg aerosol year\(^{-1}\)
What is the role of $\text{NO}_x$ in oxidative SOA formation?

Whence $\text{NO}_x$?

Combustion sources:
- vehicles
- power generation

Lightning
Soils

Highest $[\text{NO}_x]$ in urban areas:

OMI NO$_2$ column, Aura
What is the role of $\text{NO}_x$ in oxidative SOA formation?

**Whence $\text{NO}_x$?**
- Combustion sources:
  - vehicles
  - power generation
- Lightning
- Soils

In principle, can regulate these!
(can’t regulate tree VOCs)

Highest $[\text{NO}_x]$ in urban areas:
- Vehicles
- Power generation
- Lightning
- Soils
What is the role of NO\textsubscript{x} in oxidative SOA formation?

1. Suppression?

Volatile Organic Compound (VOC)

\[
\begin{align*}
\text{VOC} & \xrightarrow{\text{Oxidant}} \text{NO} \\
\text{NO} & \xrightarrow{\text{RO}} \text{RO}_{2} \\
\text{RO}_{2} & \xrightarrow{\text{HO}_{2}} \text{ROOH} + \text{O}_{2} \\
\text{RO} & \xrightarrow{\text{Isomerization}} \text{NO}_{2} \\
\text{NO}_{2} & \xrightarrow{\text{Fragments/Carbonyls}} \text{RONO}_{2} \\
\text{RONO}_{2} & \xrightarrow{\text{Less volatile products}} \\
\end{align*}
\]

Ng et al, ACP, 2007.
What is the role of NO\textsubscript{x} in oxidative SOA formation?

1. Suppression?

For VOC = \(\alpha\)-pinene, benzene, toluene, \(m\)-xylene:

- RONO\textsubscript{2} product is **more volatile** than ROOH
- \(\text{NO}_x\) **suppresses** aerosol formation

Ng et al, ACP, 2007.
What is the role of NO$_x$ in oxidative SOA formation?

1. Suppression?

Ex: $\alpha$-pinene ozonolysis

Ng et al, ACP, 2007.

What is the role of NO\textsubscript{x} in oxidative SOA formation?

2. Mixed or little effect?

What is the role of NO$_x$ in oxidative SOA formation?

3. Enhancement?

\[ \text{NO} + \text{oxyRO}_2 \rightarrow \text{RONO}_2 \]

Volatile Organic Compound (VOC)

Oxidant

More aero

Larger VOCs can switch this pattern!

Less aero

Fragments/Carbonyls

Less volatile products

Isomerization

Climate effects?
What is the role of NO$_x$ in oxidative SOA formation?

3. Enhancement?

NO + oxyRO$_2$ → RONO$_2$

Climate effects?

Volatile Organic Compound (VOC)

Oxidant

Less aero

Larger VOCs can switch this pattern! → Nitrates now more condensable
What is the role of NO$_x$ in oxidative SOA formation?

3. Enhancement?

NO$_x$ → NO + oxyRO$_2$ → RONO$_2$ → aerosol

Climate effects?

Ex: Data for photo-oxidation of longifolene
Ng et al, ACP, 2007

C$_{15}$ terpene
What is the role of NO\textsubscript{x} in oxidative SOA formation?

3. Enhancement?

\[ \text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \]

\[ \text{NO} + \text{oxyRO}_2 \]

\[ \text{NO}_3 + \text{RONO}_2 \rightarrow \text{aerosol} \]

Climate effects?

Additional possible formation pathway at night!
What is the role of NO\(_x\) in oxidative SOA formation?

3. Enhancement?

**Additional possible formation pathway at night!**

Zoom in on this aerosol formation mechanism:

\[ \text{NO}_3 + \text{VOC} \rightarrow \text{(organic nitrate) SOA} \]
NO$_3$ aerosol formation experiments in Jülich, Germany SAPHIR chamber

$$\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$$

Climate effects?

RONO$_2$

aerosol
Observed kinetics: NO$_3$ + β-pinene

\[
\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3
\]

\[
\text{NO}_3 + \text{NO}_2 \leftrightarrow \text{N}_2\text{O}_5
\]

2\textsuperscript{nd} re-charge injection of O$_3$
Observed kinetics: \( \text{NO}_3 + \beta\text{-pinene} \)

\[
\begin{align*}
\text{NO}_2 + \text{O}_3 &\rightarrow \text{NO}_3 \\
\text{NO}_3 + \text{NO}_2 &\leftrightarrow \text{N}_2\text{O}_5
\end{align*}
\]
Observed kinetics: \( \text{NO}_3^- + \beta\text{-pinene} \)
Observed kinetics: $\text{NO}_3 + \beta$-pinene
Observed chemical kinetics can be described by a simple model

\[ \text{NO}_3 + \beta\text{-pinene} \rightarrow Y \rightarrow \text{Org. nitrate, such as} \]

\[ (1-Y) \rightarrow \text{HCHO} + \text{NO}_2 + \text{ketone, such as} \]
\[ Y = \frac{\Delta M_{aero}}{\Delta HC} \]

(a corrected for wall losses)
How much aerosol could NO$_3$ + β-pinene make globally?

- Estimate by comparison to Ng et al 2008 paper on global annual source of NO$_3$ – isoprene SOA

\[
\langle S \rangle_{SOA-isop} \times \frac{Y_{NO3-bp in}}{Y_{NO3-isop}} \times \frac{E_{bp in}}{E_{isop}} = \langle S \rangle_{SOA-bp in}
\]

\[
2 - 3 \text{Tg year}^{-1} \times \frac{0.5}{0.1} \times \frac{30}{389} = 0.8 - 1.2 \text{Tg year}^{-1}
\]

If all monoterpenes have this \( Y_{SOA} \), \( \langle S \rangle_{SOA-monoterpenes} \sim 3 - 5 \text{Tg year}^{-1} \)

Global SOA source estimates:
Kanakidou et al, 2005: 12 – 70 Tg year$^{-1}$
Goldstein & Galbally, 2007: 140 – 910 Tg year$^{-1}$
A more complicated case: NO$_3$ + limonene
Limonene additions, 10 ppb and 10 ppb

\[ \text{NO}_3 + \text{limonene} \]

Graph showing mixing ratios of NO, NO\(_2\), N\(_2\)O\(_5\)/NO\(_3\), and NO\(_3\), N\(_2\)O\(_5\), and Alkyl Nitrates (ppb) over hours of experiment, 6/16/2007 & 6/17/2007.

Limonene additions, 10 ppb and 10 ppb
Evidence for secondary chemistry in \( \text{NO}_3^- + \) limonene

Limonene additions, 10 ppb and 10 ppb

\( \text{NO}_2 \), \( \text{N}_2\text{O}_5/\text{NO}_3 \)
Evidence for secondary chemistry in NO$_3$ + limonene

Limonene additions, 10 ppb and 10 ppb
2 double bonds makes life more ... interesting!
Gas/aerosol alkyl nitrate partitioning in limonene

During first limonene addition, almost all nitrate is in aerosol.
After second addition, gas phase org. nitrate builds up!

During first limonene addition, almost all nitrate is in aerosol.
Total mass yield: how strong an aerosol source?

40% mass yield; Comparable to $b$-pinene
But what about this later
$\text{NO}_3 + \text{something} \rightarrow \text{gas-phase alkyl nitrates}$?

There may be some unreacted double bonds in the aerosol!
NO₃ may also be an aerosol *sink*!

NO₃ uptake onto aerosol can be described as:

\[
k_{exp}(\text{NO₃}) = \frac{\gamma(\text{NO₃}) \cdot \bar{c}(\text{NO₃}) \cdot a}{4V}
\]

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<th>Surface</th>
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<th>Reference</th>
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<tbody>
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Laboratory results:

Can \(\text{NO₃} + \text{aerosol} \rightarrow \text{revolatilized N-containing compounds}\)?
**NO₃** may also be an aerosol **sink**!

NO₃ uptake onto aerosol can be described as:

\[
k_{\text{exp}}(\text{NO}_3) = \frac{\gamma(\text{NO}_3) \cdot \bar{c}(\text{NO}_3) \cdot a}{4V}
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**Laboratory results:**

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Can NO₃ + aerosol → revolatilized N-containing compounds?
Limonene modeling to constrain NO$_3$ uptake

Without NO$_3$ + aero → RONO$_2$(g)

With NO$_3$ + aero → RONO$_2$(g)

→ Can use empirically observed uptake coefficients to estimate atmospheric importance
So, which $\text{NO}_x$ effect wins out in the real atmosphere?

**RO + NO$_2$ suppression of aerosol yield?**

**RO + NO$_2$ enhancement?**

**NO$_3$ enhancement?**

**NO$_3$ sink of aerosol?**
Measuring NO\textsubscript{x}/aerosol effects in the real atmosphere

Reed College Air Monitoring Station, b. 2009
1000 thank-you’s to Linda George for loan of O\textsubscript{3} & NO\textsubscript{x} & nephelometer instruments!
Recent real-time data from Reed monitoring site

All data available at http://www.horizons.pdx.edu/
Observed correlation of aerosol mass with $[\text{NO}_2]$
Observed correlation of aerosol mass with $[\text{NO}_2]$ 

→ NO$_x$/aero correlation could be simply due to concentrating *everything* in days with lower planetary boundary layer.

Radar-measured wind profile, summer day 
→ daily cycle in BL height
Do better: FTIR functional group analysis of extracted aerosol samples

Soxhlet extracted into acetone/dichloromethane/hexane solvent mix, ATR-FTIR
Observed correlation of organic nitrate with \([\text{NO}_2]\)

- More RONO\(_2\) in higher-NO\(_x\) days’ aerosol: suggests nitrate enhancement
- Positive correlation between NO\(_x\) and “level of aerosol oxidation”
Are organic nitrate concentrations higher downwind of cities (NO$_x$ “point” sources on a regional scale)?

Month averaged satellite observed NO$_2$ column, March 2005

http://www.atmos.washington.edu/mm5rt/
How to get beyond the constraints of our roof deck?
Answer #1: Go in *silica*: WRF/Chem model

- Inputs: anthro & biog. emissions, reanalyzed meteorology
- Choose chemical mechanism (CBM-Z gas-phase mechanism; MOSAIC sectional aerosol); spatial domain & resolution
- Run “model world”
- Look at how chemical species are transported & reacted
- Compare to observations; adjust model mechanism

Courtesy S. Peckham, WRF Users Tutorial 2008
Chemistry movie time!
Modeled surface [Org Nitrate], ppm, 9 am PDT, Oct. 5, 2004
Modeled surface [Org Nitrate], ppm, 10 am PDT, Oct. 5, 2004
Modeled surface [Org Nitrate], ppm, 11 am PDT, Oct. 5, 2004
Modeled surface [Org Nitrate], ppm, 12 pm PDT, Oct. 5, 2004
Modeled surface [Org Nitrate], ppm, 1 pm PDT, Oct. 5, 2004
Modeled surface [Org Nitrate], ppm, 2 pm PDT, Oct. 5, 2004
Modeled surface [Org Nitrate], ppm, 3 pm PDT, Oct. 5, 2004
Organic nitrate peaks downwind and later than NO$_2$

-Peak NO$_2$ was much earlier, at 6 am PDT, and was centered around urban areas
How to get beyond the constraints of our roof deck? Answer #2: Eye in the sky!

- OMI instrument aboard Aura satellite (NO$_2$);
- MODIS instrument aboard Terra satellite (aerosol optical thickness)
How to get beyond the constraints of our roof deck? Answer #2: Eye in the sky!

Average $\text{[NO}_2\text{]}$ and aerosol optical thickness, OMI, December 2004
How to get beyond the constraints of our roof deck? Answer #2: Eye in the sky!

Hot off the press: Time-based correlation plot for Dec. 2004
How to get beyond the constraints of our roof deck? Answer #2: Eye in the sky!

Hot off the press: Time-based correlation plot for Dec. 2004

- Need longer dataset!
- Will continue seeking spatial patterns in NO$_x$/aerosol correlation; including with Δtime, correlation with upwind pixels.
- Look at seasonal patterns
Conclusions

- NO$_x$ can both suppress and enhance aerosol formation, as either NO$_2$ or NO$_3$
- Aerosol composition and NO$_2$ measurements suggest a **positive correlation** between NO$_x$ and aerosol in Portland: more enhancement than suppression
- Chemistry/meteorology modeling suggests NO$_x$-enhanced aerosol may be more pronounced downwind of urban areas; satellites are on the job!
Acknowledgements

Funding:
Reed College startup funds; Stillman Drake funds; Science Research Fellowships
PNL EMSL computing user facility

“In kind” donations:
Oregon DEQ
George and Atkinson groups at Portland State Univ.

Juelich NO₃ intercomparison campaign team esp. Ron Cohen, Drew Rollins, Paul Wooldridge, Astrid Kiendler-Scharr, and Steve Brown

Holly Neill and Josh Katz

Jess Tobin and Anna Stonestrom

Linda George & her O₃ and NOₓ emporium

Li Zha
Thank you!

Volatile Organic Compounds (VOCs) → OH, O₃, NO₃ → ... → NOₓ → oxyVOCs (incl. nitrates) → aerosol → Climate effects?

Juliane L. Fry
fry@reed.edu
Assistant Professor of Chemistry
Reed College, Portland, OR
Extra slides
Motivation: Aerosol-climate interaction

Direct effect: Aerosols scatter or absorb sunlight

Semi-direct effect: Aerosol absorption heats atmosphere, reducing cloud cover

Indirect effects: Aerosols modify cloud properties to more numerous, smaller CCN
  “1st indirect effect”: Make clouds brighter
  “2nd indirect effect”: Make clouds longer-lived
Motivation: Focus on organic (carbonaceous) aerosol

“Uncertainties [in aerosol direct radiative forcing] remain relatively large … These arise from difficulties in determining the concentration and radiative characteristics of atmospheric aerosols and the fraction of the aerosols that are of anthropogenic origin, particularly the knowledge of the sources of carbonaceous aerosols.” – IPCC TAR, 2001

- Organic aerosol (OA) plays an important role in both direct and indirect forcing
- According to model, OA contributes 20-50% of total fine aerosol mass at continental mid-latitudes & up to 90% over tropical forests
Lots of unexplained SOA; likely highly oxidized

Diesel organic aerosol
- red bars: data from dilution experiment
- hatched bars: “intermediate volatility” – not measured, but extrapolated.

UV irradiation of diesel OA
- Unexplained SOA not from traditional precursors
- AMS spectrum looks like oxidized OA

How much SOA could there be?

Losses of ~ ½ of nonmethane organic carbon in the atmosphere is unaccounted for!
→ Hypothesis: this unexplained loss is due to formation of SOA.

Reminder: Kanakidou et al, 2005:
SOA source: 12 – 70 Tg aerosol year\(^{-1}\)

New SOA source estimates:
- 510-910 TgC year\(^{-1}\) from VOC mass balance
- 225-575 TgC year\(^{-1}\) from estimated wet & dry deposition + oxidation of SOA
- 140-540 TgC year\(^{-1}\) from sulfate sources + measured mass ratios
- 223-615 TgC year\(^{-1}\) from assumed SOA vertical distribution and lifetime

Source: Goldstein and Galbally, ES&T 2007.
Why focus on nighttime NO$_3$ + biogenic VOCs?

- NO$_3$ is the major nighttime product of NO$_x$; → anthropogenically controlled

- Biogenic VOCs, such as are copiously emitted by trees (In US: biogenics 30-60 Tg/yr, anthropogenic VOCs 27 Tg/yr; Nighttime [terpenes] up to 2 ppb), and highly reactive with NO$_3$ (relative to O$_3$)

- Requires both biogenic (natural) emissions and anthropogenic NO$_x$ pollution!
Large NO$_3$–initiated SOA formation resolves a paradox: Modern carbon / anthropogenic source of SOA

$^{14}$C measurements suggest modern, i.e., *biogenic*, sources of SOA, but variability is highly correlated to *anthropogenic* species

**Potential resolution:** NO$_3$ + biogenic VOC has high SOA yield

*Atmospheric* NO$_3$ aerosol source:

- 60 ppb O$_3$, 1 ppb NO$_2$ $\rightarrow$ 0.85 ppb total NO$_3$ source
- If only 10% becomes SOA: 0.7 $\mu$g/m$^3$ aerosol night$^{-1}$ (~few $\mu$g/m$^3$ bkg)

→ Chamber experiments at Jülich, Germany, June 2007
Thermal Dissociation – Laser Induced Fluorescence (NO2-TD-LIF) measurement of NOy

Unique & highly sensitive NOy instrument!

Ambient channel: NO₂

Δ_{180-40} = ΣPAN + N₂O₅

Δ_{340-180} = ΣAN

Δ_{600-340} = HNO₃ + N₂O₅ + NO₃
A well-instrumented chamber!

- NOAA NO$_3$/N$_2$O$_5$. Thanks to: Steve Brown, Hendrik Fuchs, Bill Dube

- AMS Nitrate (NO$_3^-$), and total aerosol mass. Thanks to: Astrid Kiendler-Scharr, Amewu Mensah

- PTR-MS hydrocarbon concentrations. Thanks to Ralf Tillmann & Robert Wegener

- Our NO$_y$: NO$_2$, PANs, Alkyl nitrates, and HNO$_3$