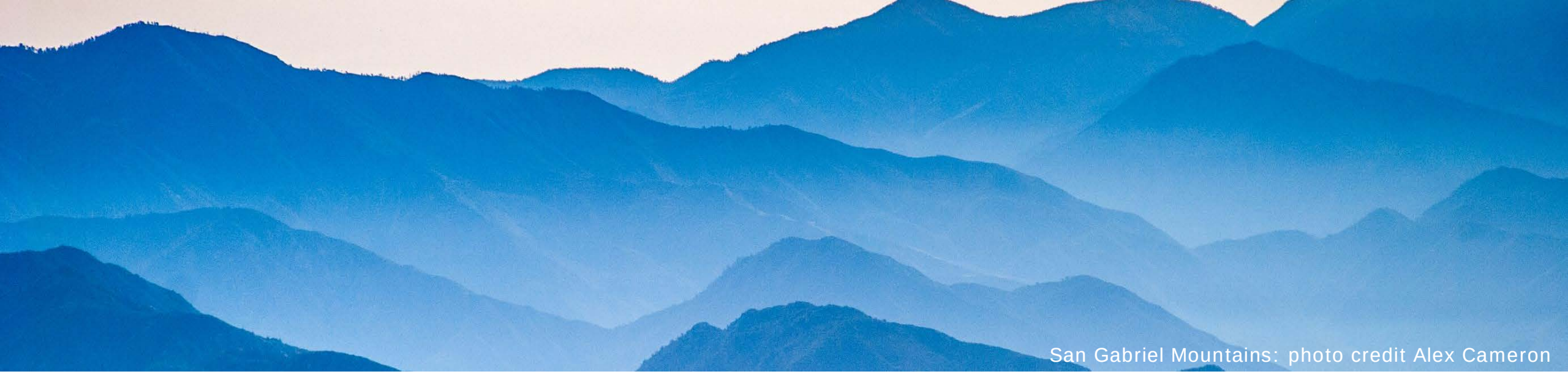
San Gabriel Mountains: photo credit Alex Cameron

The Challenge of Modeling the Chemistry of Ozone

Greg Yarwood

gyarwood@ramboll.com

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Health Effects Institute Annual Conference
May 2, 2017

Topics

Chemical life cycle of nitrogen oxide (NO_x) emission

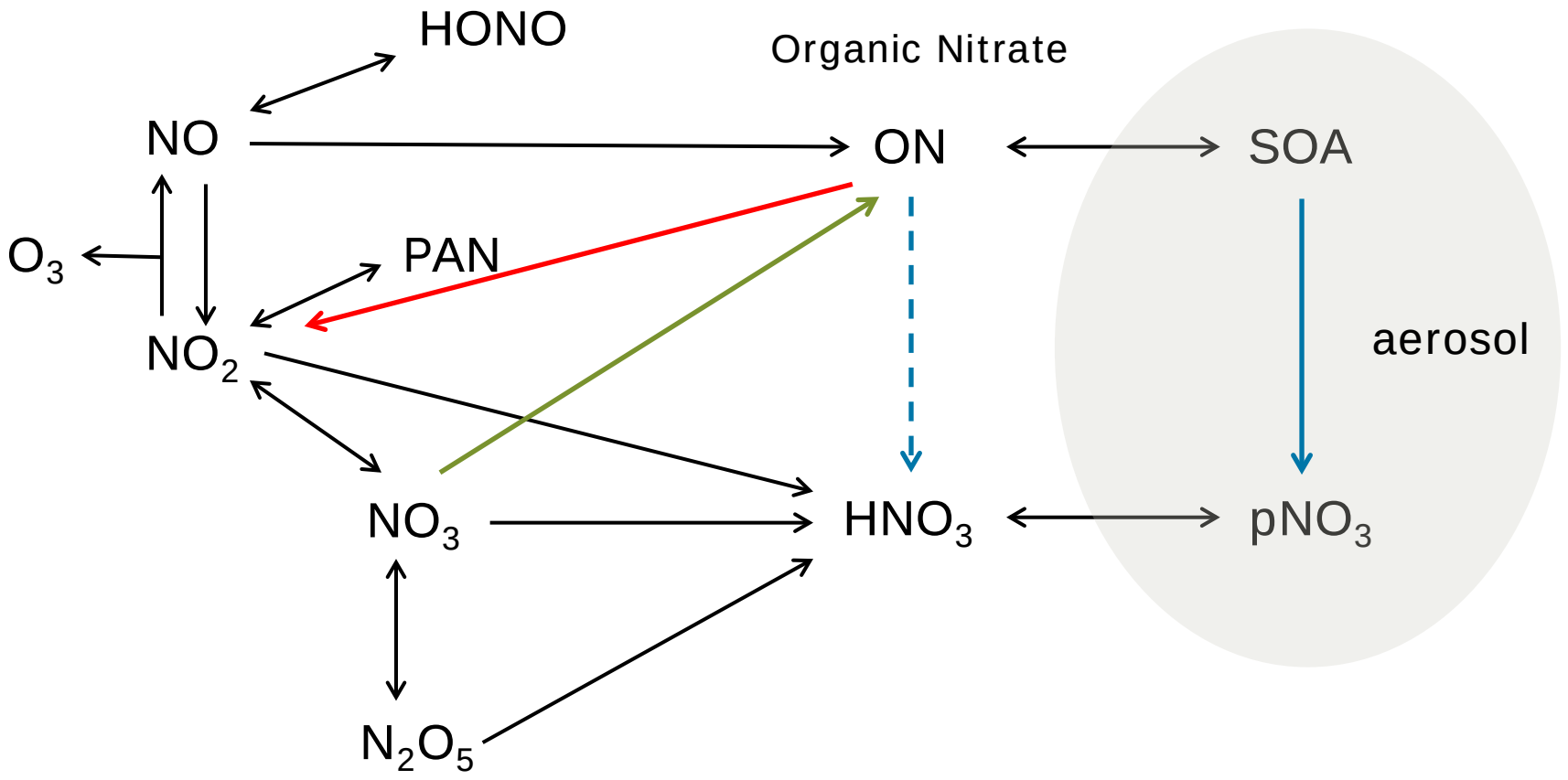
Chemical controls over NO_x removal and potential for NO_x recycling

NO_x influence on distributions of ozone concentration

Organic nitrate (ON) removal by condensed-phase hydrolysis

Nitrate radical + terpene reactions

Chemical life cycle of NOx emission



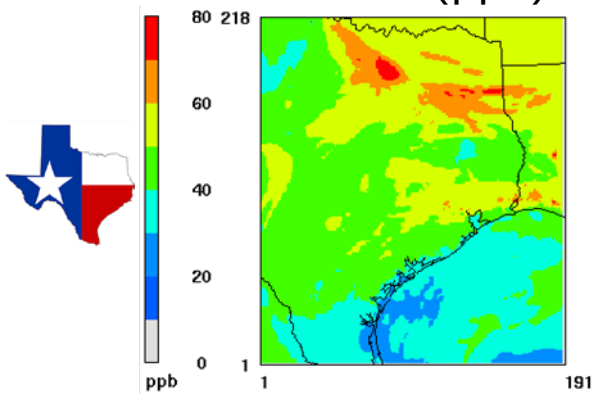
NOx recycling

ON hydrolysis

NO3 + terpene

Daytime NO_x chemical removal: Urban / rural differences

Ozone (ppb)

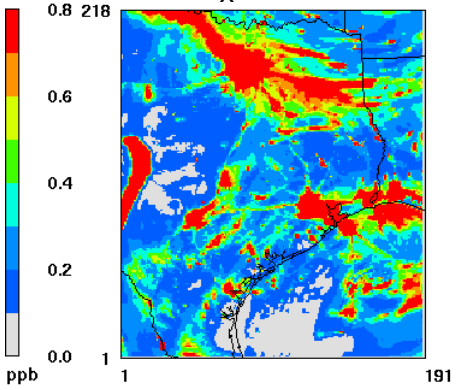


Removing NO_x stops it from participating in ozone formation

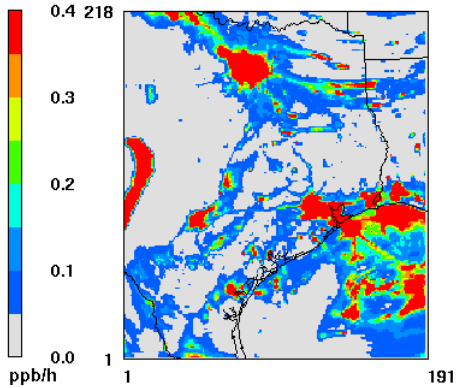
Urban (higher NO_x): three pathways all active

Rural (low NO_x): organic nitrate (ON) pathway becomes dominant

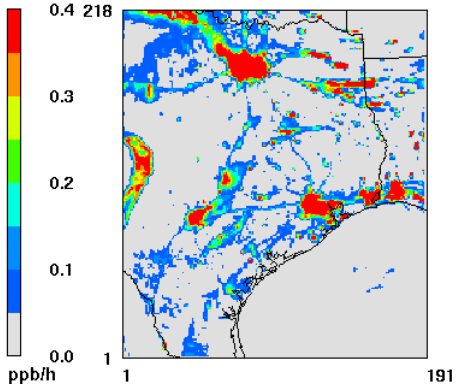
NO_x (ppb)



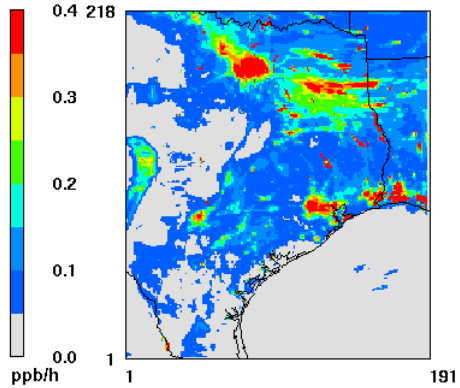
NO_x to HNO_3 (ppb/h)



NO_x to PAN (ppb/h)



NO_x to ON (ppb/h)

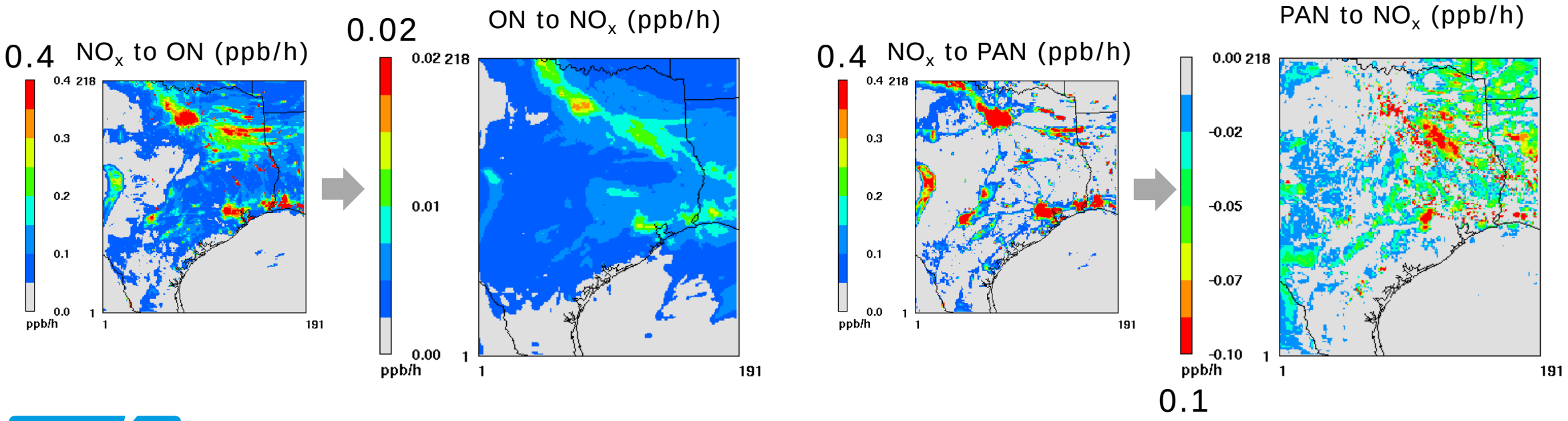


NO_x recycling: Distributing NO_x to rural areas

Chemical reactions of ON, HNO_3 and PAN can release NO_x: termed "NO_x recycling"

Uncertain magnitude of NO_x recycling from ON:
- Extent of ON partitioning to aerosol
- Rate of ON hydrolysis within aerosol

NO_x recycling from PAN mediated by PAN decomposition: $T_{1/2}$ of 40 mins @ 298K vs. 40 hours at 273K



Modeling H4MDA8 Ozone variation with NO_x and VOC

Atmospheric Environment 101 (2015) 209–216

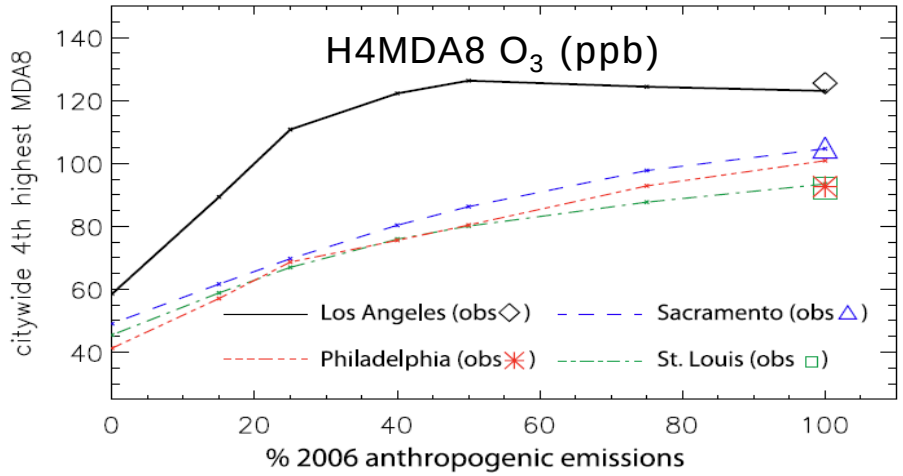
This research funded by the American Petroleum Institute (API)

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Emission reductions and urban ozone responses under more stringent US standards

Nicole Downey [a, *], Chris Emery [b], Jaegun Jung [b], Tanarit Sakulyanontvittaya [b], Laura Hebert [a], Doug Blewitt [a], Greg Yarwood [b]



- Nationwide photochemical modeling (WRF/CAMx)
- Quantify emission reductions from 2006 to attain various potential National Ambient Air Quality Standards (NAAQS)
- Novel application of ozone sensitivity (DDM) allows continuous and independent variation

$$\Delta O_3 = \Delta N S_N^{(1)} + \frac{1}{2}\Delta N^2 S_N^{(2)} + \Delta V S_V^{(1)} + \frac{1}{2}\Delta V^2 S_V^{(2)} + \Delta N \Delta V S_{NV}^{(2)},$$

where

$$S_N^{(1)} = \partial O_3 / \partial NOx$$
$$S_V^{(1)} = \partial O_3 / \partial VOC$$
$$S_N^{(2)} = \partial^2 O_3 \Big/ \partial NOx^2$$
$$S_V^{(2)} = \partial^2 O_3 \Big/ \partial VOC^2$$
$$S_{NV}^{(2)} = \partial^2 O_3 \Big/ \partial NOx\, \partial VOC$$

- Provides long (annual, ozone season) **simulated ozone time-series** at adjustable NO_x & VOC emission level

H4MDA8 = annual fourth highest maximum daily 8-hour average

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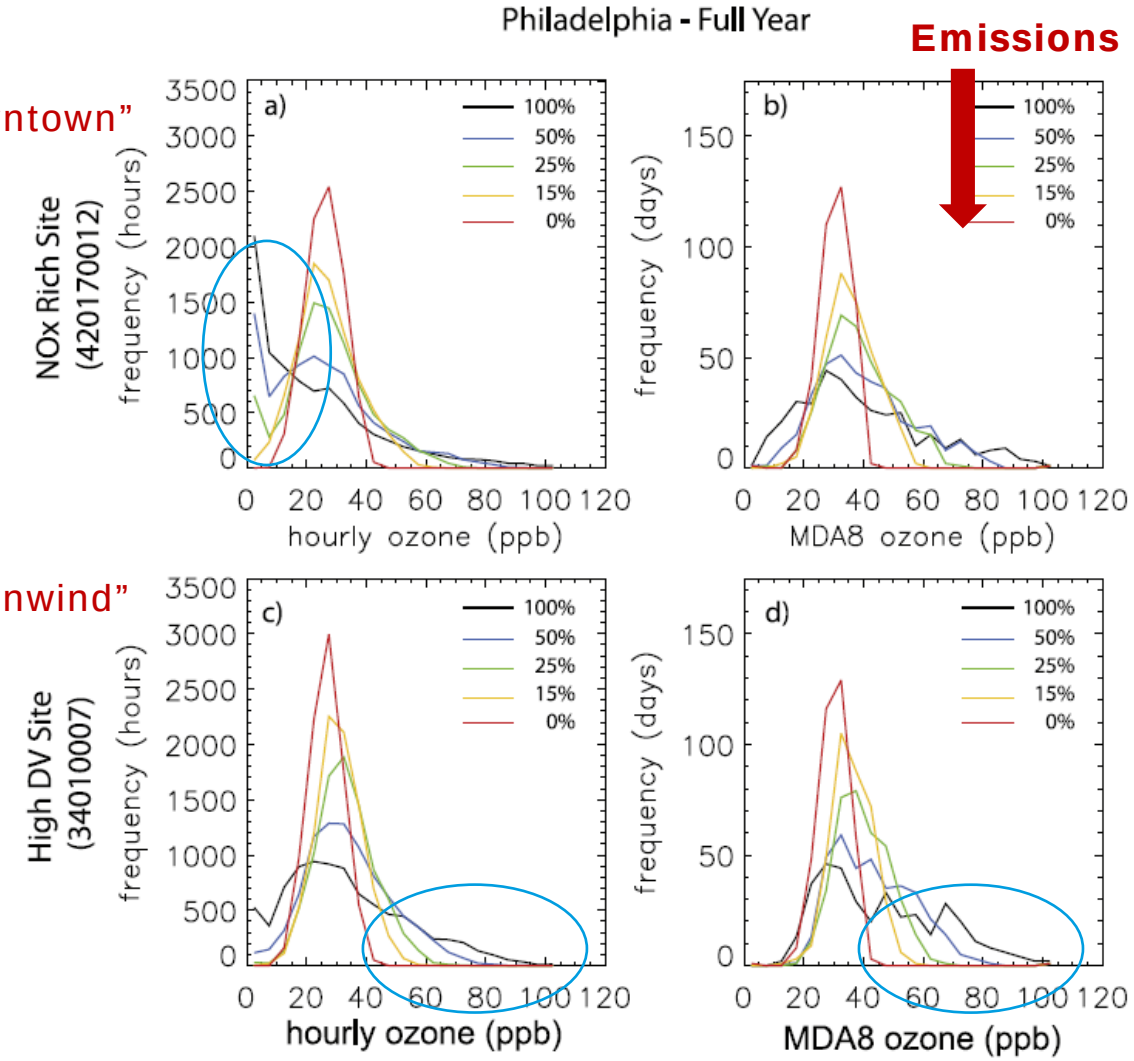
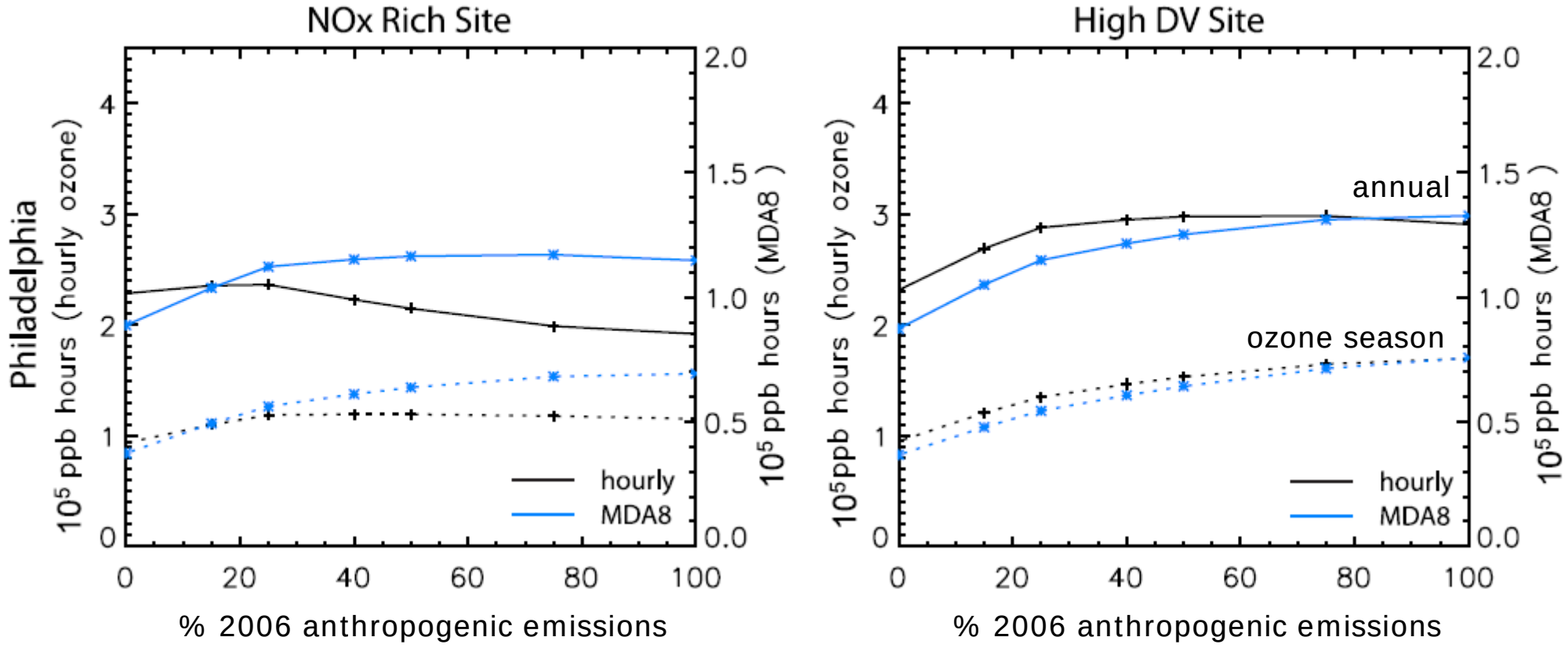
Reducing NO_x changes the ozone distribution

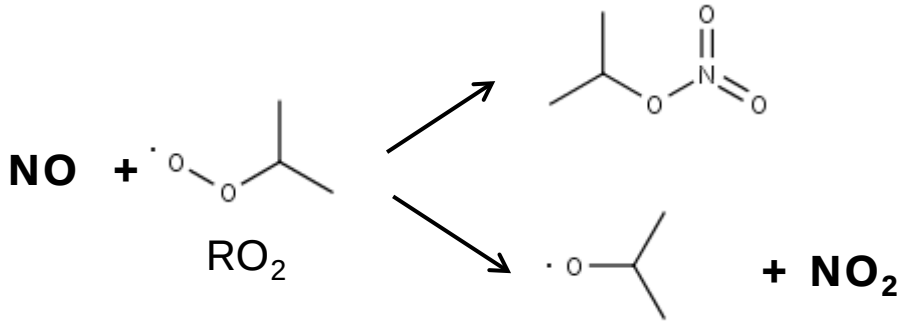


- Emission reductions truncate the high tail of maximum daily 8-hour (MDA8) and hourly ozone
- Emission reductions also can truncate a low tail of suppressed ozone
  - Especially "downtown"
  - More pronounced for hourly than MDA8 ozone
  - More impact for full year than ozone season (not shown)
- As anthropogenic emissions -> zero the distribution of background ozone appears

Ozone exposure (ppb hours) recalcitrant to reducing emissions



ON formation and examples

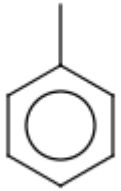


Precursor

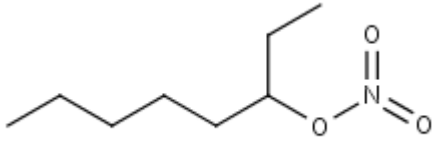
n-octane

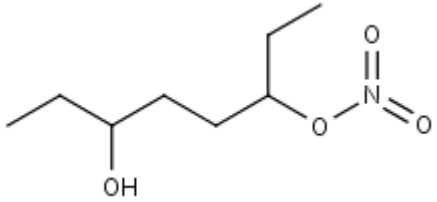
1-butene

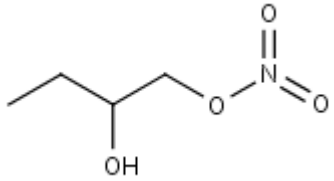
toluene

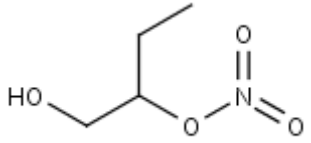


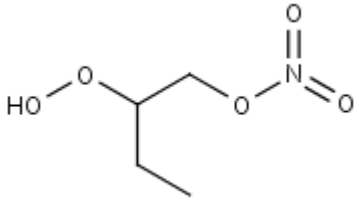
Organic Nitrate

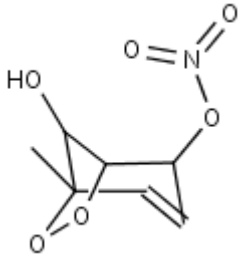








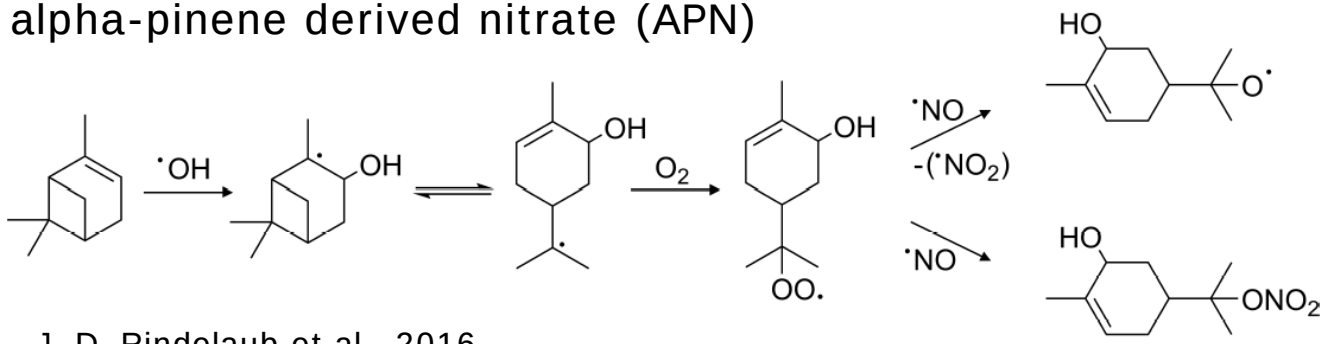




From the Master Chemical Mechanism (MCM) version 3.3.1

Organic nitrates removed by condensed-phase hydrolysis

alpha-pinene derived nitrate (APN)



J. D. Rindelaub et al., 2016

APN

- acid-catalyzed mechanism
- nitric acid formed
- rapid for APN at relevant pH
- consistent with findings from field studies in south eastern United States
- slower for small ON molecules

Table 2. The hydrolysis lifetimes of isopropyl nitrate (IPN), isobutyl nitrate (IBN), and the α-pinene-derived nitrate (APN) at varying pH.

	Lifetime		
pH	IPN	IBN	APN
0.25	28 h	23 h	8.3 min
1.0	–	–	44 min
1.7	35 days	33 days	–
2.5	–	–	33 min
4.0	30 days	28 days	1.3 h
6.9	> 8 months	> 8 months	8.8 h

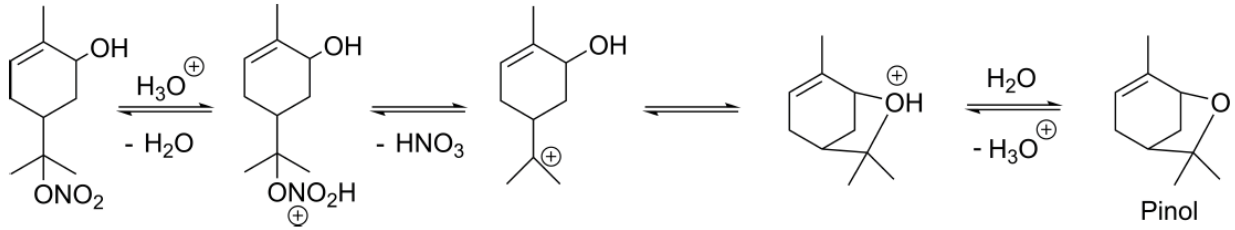
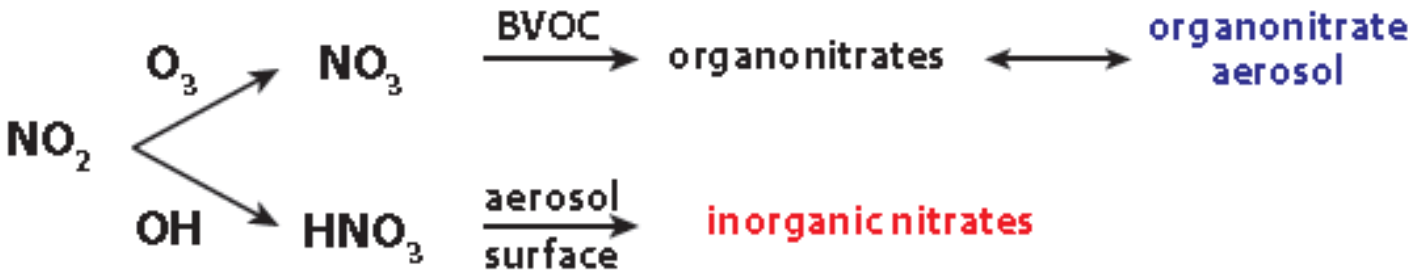


Figure 6. The proposed acid-catalyzed hydrolysis mechanism of an α-pinene-derived nitrate.

Nitrate radical + terpenes: Remove NO_x and form secondary organic aerosol (SOA)



B. R. Ayres et al., 2015

- Terpenes dominate NO_3 radical loss at night and are important during the day
- Inferred molar yield of aerosol-phase monoterpene ON of 23–44 %
- ON comprised 30–45% of the total reactive nitrogent (NO_y) budget during Southern Oxidant and Aerosol Study (SOAS)

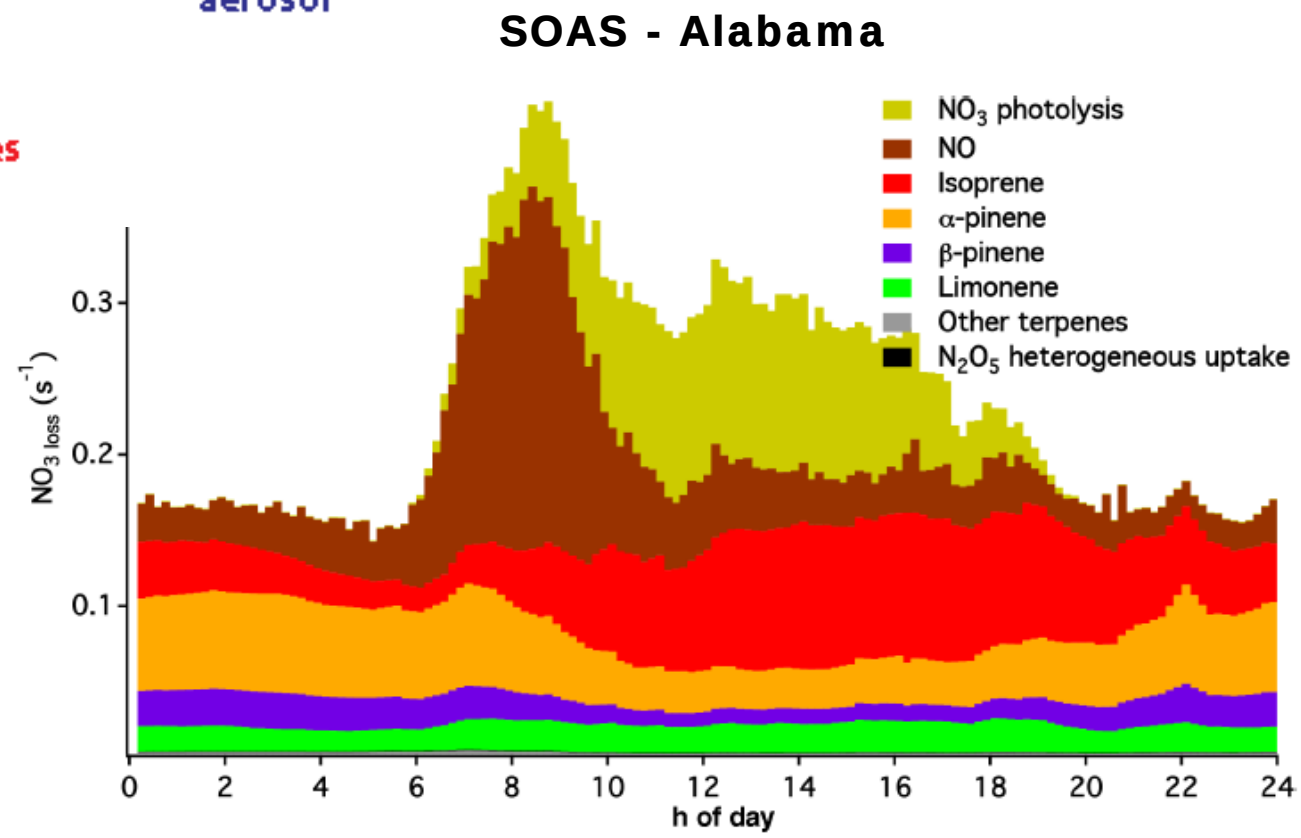


Figure 4. Average diurnal profile of NO_3/N_2O_5 losses 1 June–

Thank You

Reminders:

- NO_x recycling: Distributing NO_x to rural areas
- Ozone *exposure* recalcitrant to reducing NO_x emissions
- Organic nitrates removed by condensed-phase hydrolysis
- Nitrate radical + terpenes: Removing NO_x and forming SOA