The Seasonality of Tropospheric Ozone and Reactive Nitrogen: From Measurements to Models

Erin E. McDuffie\textsuperscript{1,2,3}, Steven S. Brown\textsuperscript{1,3}, Jessica B. Gilman\textsuperscript{2,3}, Brian M. Lerner\textsuperscript{2,3}, Peter M. Edwards\textsuperscript{4}, Dorothy Fibiger\textsuperscript{5}, William P. Dubé\textsuperscript{2,3}, Michael Trainer\textsuperscript{3}, Wayne M. Angevine\textsuperscript{2,3}, Stuart McKeen\textsuperscript{2,3}, Daniel E. Wolfe\textsuperscript{6}, Alex G. Tevlin\textsuperscript{7}, Jennifer Murphy\textsuperscript{7}, Emily V. Fischer\textsuperscript{8}, Felipe Lopez-Hilfiker\textsuperscript{8}, Joel A. Thornton\textsuperscript{8}, Jeff Peischl\textsuperscript{2,3}, Andrew O. Langford\textsuperscript{2,3}, Christoph J. Senff\textsuperscript{2,3}, John S. Holloway\textsuperscript{2,3}, Eric J. Williams\textsuperscript{3}, Joost deGouw\textsuperscript{1,2,3}, Thomas B. Ryerson\textsuperscript{3}, Kenneth Aiken\textsuperscript{2,3}, Samuel Hall\textsuperscript{10}, Kirk Ullmann\textsuperscript{10}, Kathy O. Lantz\textsuperscript{10}, Bill Kuster\textsuperscript{2,3}, Rebecca Hornbrook\textsuperscript{10}, Eric Apel\textsuperscript{10}, Allan Hills\textsuperscript{10}

\textsuperscript{1}Department of Chemistry, University of Colorado, \textsuperscript{2}Cooperative Institute for Research in Environmental Sciences, University of Colorado, \textsuperscript{3}NOAA, Chemical Sciences Division, \textsuperscript{4}Department of Chemistry, University of York, United Kingdom, \textsuperscript{5}Geospace Postdoctoral Fellow, \textsuperscript{6}NOAA, Physical Sciences Division, \textsuperscript{7}Department of Chemistry, University of Toronto, Canada, \textsuperscript{8}Department of Atmospheric Science, Colorado State University, \textsuperscript{9}Department of Atmospheric Sciences, University of Washington, \textsuperscript{10}Atmospheric Chemistry Observations and Modeling Laboratory, NCAR, \textsuperscript{11}NOAA, Global Monitoring Division

Outline:
1) Project #1 – Colorado Emissions & Ozone Photochemistry
2) Project #2 – Wintertime Reactive Nitrogen Partitioning

3\textsuperscript{rd} Year Analytical Seminar
March 14, 2016
Tropospheric Ozone: Motivation

Greenhouse Gas + Health Hazard $\rightarrow$ Regulated by US EPA

Photochemical Source:

‘Oxidized VOCs’ + $\text{NO}_x \rightarrow \text{O}_3$
Tropospheric Ozone: Photochemistry

NO\textsubscript{x} Emissions

\[ \text{NO} \rightarrow \text{O}_3 \rightarrow \text{NO}_2 \rightarrow \text{NO}_x \rightarrow \text{OH} \rightarrow \text{NO}_x \]

Sunlight, O\textsubscript{2}
Tropospheric Ozone: Photochemistry

VOC Emissions

\[ \text{VOC} \xrightarrow{\text{OH}} \text{RO}_2^* \xrightarrow{O_2} \text{RO}^* \]

NO\textsubscript{x} Emissions

\[ \text{NO} \xrightarrow{\text{Sunlight, O}_2} \text{NO}_2 \xrightarrow{\text{OH}} \text{NO}_x \]

\[ \text{O}_3 \]
Tropospheric Ozone: Photochemistry

VOC Emissions

VOC $\xrightarrow{\text{OH}}$ RO$_2^\cdot$ $\xrightarrow{\text{O}_2}$

NO$_x$ Emissions

NO $\xrightarrow{\text{Sunlight, O}_2}$ NO$_2$

NO$_2$ $\xrightarrow{\text{OH}}$ NO$_3$

Sunlight, O$_2$

O$_3$
Tropospheric Ozone: Photochemistry

Radical Recycling

=More Efficient O₃ Production

VOC Emissions

NOₓ Emissions

Local/Regional Emission Sectors

O₃

Sunlight, O₂

O₂

OH

O₂

OH

OH

RO₂⁺

RO⁺

NO

NO₂

NO₂⁻
Global average surface temperature increased by 0.074°C per decade when estimated by a linear trend for the 100 year period, 1906–2005 [Intergovernmental Panel on Climate Change (IPCC), 2007], while the rate of increase since the late 1970s is 0.15–0.20°C per decade [Hansen et al., 2010]. As global temperatures have increased since the 19th century so too has the global tropospheric ozone burden, primarily due to rising anthropogenic emissions of ozone precursors [Lamarque et al., 2005]. Based on the model studies of ozone response to future climate change, one might assume that past ozone changes have also been influenced by climate change since the 19th century. A recent intercomparison of 10 atmospheric chemistry models run with year 2000 emissions but with 2000s and 1850s climate shows a range of responses of tropospheric ozone to the observed temperature increase [Stevenson et al., 2012]. Six out of 10 models indicate ozone decreases at the surface of the northern hemisphere midlatitudes due to observed climate change, but the decreases are small (<2 ppbv). Four out of 10 models indicate regions of both positive and negative surface ozone changes, but these changes are also small (<2 ppbv). In the free troposphere of northern midlatitudes the models indicate a range of ozone changes that are also small (<2 ppbv).

Given the small and variable response of modeled ozone to observed climate change from the 1850s to 2000s we do not expect a strong impact from climate change over the much shorter time periods of 1990–2010 (surface ozone changes).
Increased Western Wildfire Activity
• Pollution Transport from Asia
• Changes in Regional Urban and Oil and Natural Gas (O&NG) Emissions

Proposed Explanations:

- NO\textsubscript{x} Emission Reductions

Cooper, O., R. et al. 2012, J. Geophys. Res. 117, D22307
Colorado Northern Front Range (NFR)

- Fort Collins
- Greeley
- Boulder
- Denver
- BAO

> 27,000 Active Oil and Natural Gas Wells

Urban NO$_x$ + VOC

Urban Boundaries
- Active Oil&Gas Wells
- Agriculture
- Power Plants
- Measurement Site

Colorado Location

Field Measurements | OH Reactivity | O$_3$ Production Efficiency | Box-Model
Colorado Northern Front Range (NFR)

- > 27,000 Active Oil and Natural Gas Wells
- Urban NO\textsubscript{x} + VOC
- BAO
- Fort Collins
- Greeley
- Boulder
- Denver
- 300m Tower
- Urban Boundaries
- Active Oil&Gas Wells
- Agriculture
- Power Plants
- Measurement Site
Data: NO\textsubscript{x}, NO\textsubscript{y}, O\textsubscript{3}, Speciated VOCs, CH\textsubscript{4}, CO, NH\textsubscript{3}, j(NO\textsubscript{2}), albedo, meteorological data

**2014**
FRAPPE/DISCOVER-AQ (NO\textsubscript{y}, no speciated VOCs)

**2012** – SONNE (Speciated VOCs, no NO\textsubscript{y})
Composition at BAO characteristic of Urban and O&NG Emission Sectors

2014 Chemical Tracers

Oil and Natural Gas: Enhanced CH$_4$

- Average
- 90$^{th}$, 10$^{th}$ Percentiles
- 75$^{th}$, 25$^{th}$ Percentiles

Urban: NO$_x$ and Enhanced CO
Composition at BAO characteristic of Urban and O&NG Emission Sectors

**2012 VOCs**

- Bar Height: Mean Carbon Mixing Ratio
  - Alkanes
  - Alkenes/Alkynes
  - Aromatics
  - Aldehydes/Ketones
  - Alcohols
  - Biogenic VOC

**O&NG VOC Contribution**


**Average Fractional Contribution**

- Alkanes: 82%
- Alkenes/Alkynes: 7%
- Aromatics: 6%
- Aldehydes/Ketones: 3%
- Alcohols: 1%
- Biogenic VOC: 1%
OH Reactivity (OHR):

\[ \Sigma(k_{\text{OH+VOC}} \times [\text{VOC}]) \]

Previously used in O&NG focused O\(_3\) studies
### OH Reactivity (OHR):

Commonly used as a metric for ‘O₃ forming potential’

\[
\Sigma (k_{\text{OH}+\text{VOC}} \times [\text{VOC}])
\]

![Chemical reaction diagram showing VOC and NOx emissions leading to O₃ formation](image-url)

Previously used in O&NG focused O₃ studies
OH Reactivity (OHR):

- Barnett Basin, TX
  - O&NG: 13-20%
  - Biogenic: 70%

- Marcellus Basin, PA
  - O&NG: 7%
  - Biogenic: 47%

O&NG VOCs contribute ~ 50% to OH Reactivity

OPE: Slope of $O_x$ ($= O_3 + NO_2$) against $NO_z$ ($= NO_y - NO_x$) as a measure of the number of $O_3$ molecules produced per $NO_x$ molecules oxidized

**NOT** previously used in O&NG focused $O_3$ studies
OPE: Slope of $O_x$ (\(= O_3 + NO_2\)) against $NO_z$ (\(= NO_y - NO_x\)) as a measure of the number of $O_3$ molecules produced per $NO_x$ oxidized.

2014: 12pm-6pm (MDT) 16 July-15 August

Average of 80 Individual OPEs = 5.3 ± 3.6 ppbv/ppbv
OPE vs. Wind Direction

Urban and O&NG OPEs not distinguished by wind direction

OPE Differences:
1) Obscured by air mixing
2) < 1.4 ppbv/ppbv
OPE vs. Chemical Tracers

- O&NG: Enhanced CH₄

- Urban: Enhanced CO and NOₓ

Combined Wind Direction & Chemical Tracer Analysis Results:
Urban and O&NG OPEs are not distinguished by simple chemical tracers

1) Mixed air masses at BAO
2) O&NG and Urban sectors do not uniquely influence OPE by > 1.4 ppbv/ppbv

Photolysis – NCAR’s TUV \( \rightarrow \) Scaled to \( j(\text{NO}_2)/j(\text{O}^1\text{D}) \) observations
Chemistry – Master Chemical Mechanism (MCM) \( \rightarrow \) 4002 species, 15555 reactions

Wintertime \( \text{O}_3 \) Production in Utah’s Uintah O&NG Basin

\textbf{NOT} previously used in O&NG focused \textbf{SUMMER} \( \text{O}_3 \) studies
On Average, Oil and Natural Gas (O&NG) VOC Emissions Contribute ~19%* to Maximum O$_3$ Photochemically Produced at BAO

The Northern Front Range of Colorado is in a NO$_x$ Sensitive Regime
**Modeled OPE**: Dependent on NO\textsubscript{x} mixing ratio and temperature

**Average OPE vs Base Case**

**Base Case vs No O&NG VOCs**

1) Modeled OPEs within 1 standard deviation of Observed 2014 Average (accurate Base Case)

2) O&NG Emissions influence OPE by ~1.0 ppbv/ppbv (consistent with OPE vs wind direction analysis)
Project #1: Summary and Conclusions

Regional O\textsubscript{3} photochemistry is dependent on local NO\textsubscript{x} and VOC emission sources

BAO experiences both O&NG & urban emissions

At BAO:
1) O\textsubscript{3} production is sensitive to NO\textsubscript{x} emissions

2) O&NG VOC emissions contribute:
   ~ 80% to observed carbon mass (ppbC)
   ~ 50% to O\textsubscript{3} forming potential (OHR)
   ~ 19% to maximum photochemical O\textsubscript{3}
   ~ 1.0 ppbv/ppbv OPE
Project #2: Influence of Reactive Nitrogen Chemistry on Wintertime Tropospheric O$_3$
Project #2: Quantify the Influence of Heterogeneous Reactive Nitrogen Mechanisms on Winter O$_3$

Tropospheric Ozone: Dark Chemistry

VOC Emissions

VOC $\rightarrow$ OH $\rightarrow$ RO$_2^\cdot$ $\rightarrow$ RO$^\cdot$

$\rightarrow$ NO

NO$_x$ Emissions

$\rightarrow$ NO

$\rightarrow$ NO$_2$

$\rightarrow$ OH $\rightarrow$ NO$_2$

Sunlight, O$_2$

$\rightarrow$ O$_3$
Tropospheric Ozone: Dark Chemistry

\[ \text{NO} \xrightarrow{\text{Sunlight, O}_2} \text{NO}_2 \xrightarrow{\text{NO} \text{Emissions}} \text{NO}_2 \xrightarrow{\text{NO} \text{Emissions}} \text{NO} \xrightarrow{\text{Sunlight, O}_2} \text{O}_3 \]
Consequences for:

- Wintertime tropospheric O\textsubscript{3} budget
- Lifetime and distribution of NO\textsubscript{x}, O\textsubscript{3}, and additional tropospheric oxidants (i.e. OH)
- Magnitude and mechanisms for sources of tropospheric halogens
Consequences for:

• Wintertime tropospheric O₃ budget
• Lifetime and distribution of NOₓ, O₃, and additional tropospheric oxidants (i.e. OH)
• Magnitude and mechanisms for sources of tropospheric halogens
Heterogeneous N$_2$O$_5$ Processes: Key Parameters

Remaining Scientific Uncertainties: $\gamma$, $\phi$ in different ambient environments (e.g. temperature, RH, aerosol composition)

...Approach... field data to constrain values
Campaign: Wintertime Investigation of Transport, Emissions, and Reactivity (WINTER)

February – March 2015
• 6 weeks – 13 research flights
  • Day and Night
  • Coastal and Interior Environments

6-Channel CRD:
$\text{N}_2\text{O}_5$, $\text{NO}_3$, $\text{NO}_x$, $\text{O}_3$, $\text{NO}_y$
Heterogeneous $\text{N}_2\text{O}_5$ Processes: Observed Variability

3 Examples from WINTER:
Heterogeneous N$_2$O$_5$ Processes: Observed Variability

3 Examples from WINTER:

*HNO$_3$ and ClNO$_2$ from University of Washington CIMS

N$_2$O$_5$ as NO$_x$ reservoir

US East Coast
Heterogeneous $\text{N}_2\text{O}_5$ Processes: Observed Variability

3 Examples from WINTER:

- Feb. 24th
  - $\text{N}_2\text{O}_5$ as $\text{NO}_x$ reservoir

- Feb. 23rd
  - Conversion of $\text{N}_2\text{O}_5$ to $\text{HNO}_3$

*H$_3$NO$_3$ and ClNO$_2$ from University of Washington CIMS
Heterogeneous $N_2O_5$ Processes: Observed Variability

3 Examples from WINTER:

- Feb. 24th: $N_2O_5$ as $NO_x$ reservoir
- Feb. 23rd: $N_2O_5$ conversion to $HNO_3$
- Feb. 8th: $N_2O_5$ conversion to $ClNO_2$

*HNO_3 and ClNO_2 from University of Washington CIMS
Project #2: Summary and Future Work

WINTER data show: $\gamma$ and $\phi$ are highly variable

Scientific Questions
1) What drives Reactive Nitrogen Partitioning (i.e. differences in $\gamma$ and $\phi$)?
2) Can we associate certain partitioning with certain ambient conditions?
3) Can we use conditions/chemistry to predict $\gamma$ and $\phi$?

Methods
1) Derive $\gamma$, $\phi$ from $N_2O_5$, ClNO$_2$, aerosol observations
2) Box - Model $\gamma$

Model Output:

$$k(N_2O_5) = \frac{1}{4} \cdot c \cdot S_A \cdot \gamma(N_2O_5)$$
Questions?

*NYC from the C130 cockpit, photo courtesy of Joel Thornton*