What are Dr. Seuss's favorite air pollutants?

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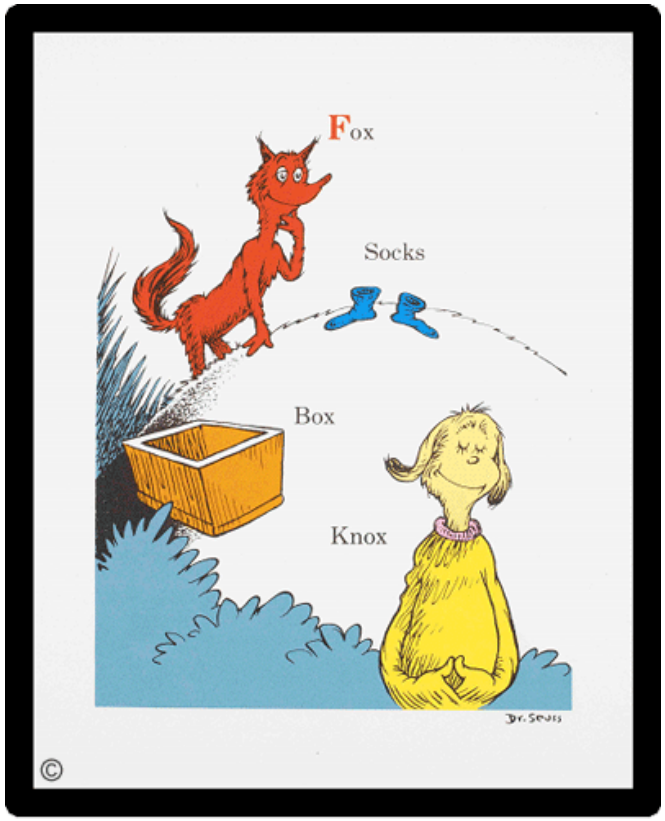

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NO_x and SO_x

NO_x and Ambient Air Chemistry as it relates to the New NO_2 1-Hour Standard

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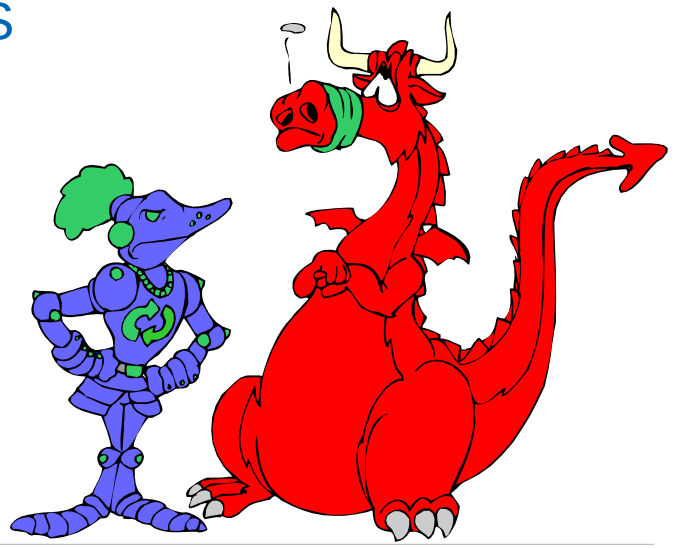
NO_2 1-Hour Standard

- EPA recently revised the primary NAAQS (National Ambient Air Quality Standards) to include a 100 ppb averaged hourly standard
  - More stringent, more complicated standard
  - More modeling required and more difficult to prove compliance

- New and existing sources are required to show that they do not cause a significant contribution to a violation of NAAQS



NO_x Introduction

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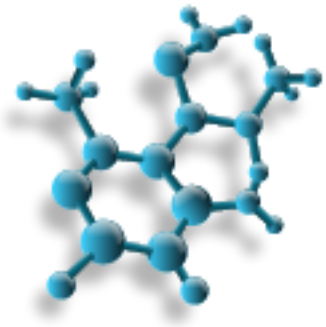
- Nitrogen Oxides (NO_x) are a family of gases formed during combustion and include:

NO NO_2 N_2O NO_3

N_2O_3 N_2O_4 N_2O_5

- The majority of NO_x however are in the form of NO and NO_2

- Most NO_x combustion emissions are in the form of NO



NO_x In-Stack Air Chemistry

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- Two major types of NO_x Formation
  - Primary source is thermal NO_x
  - Secondary source is fuel-bound NO_x

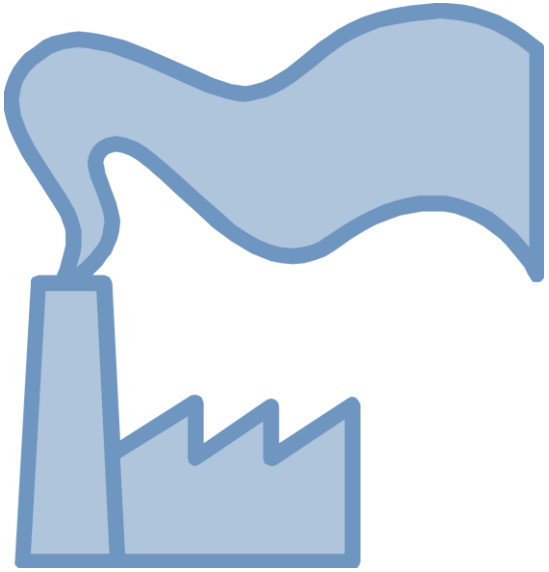
- Thermal NO_x Formation

$$N_2 + O \leftrightarrow NO + N$$

$$N + O_2 \leftrightarrow NO + O$$

$$N + OH \leftrightarrow NO + H$$

$$2NO + O_2 \leftrightarrow 2NO_2$$



NO_x Ambient Air Chemistry

- NO and NO_2 react with a variety of constituents in ambient air
- Three main reactions that reside in equilibrium:

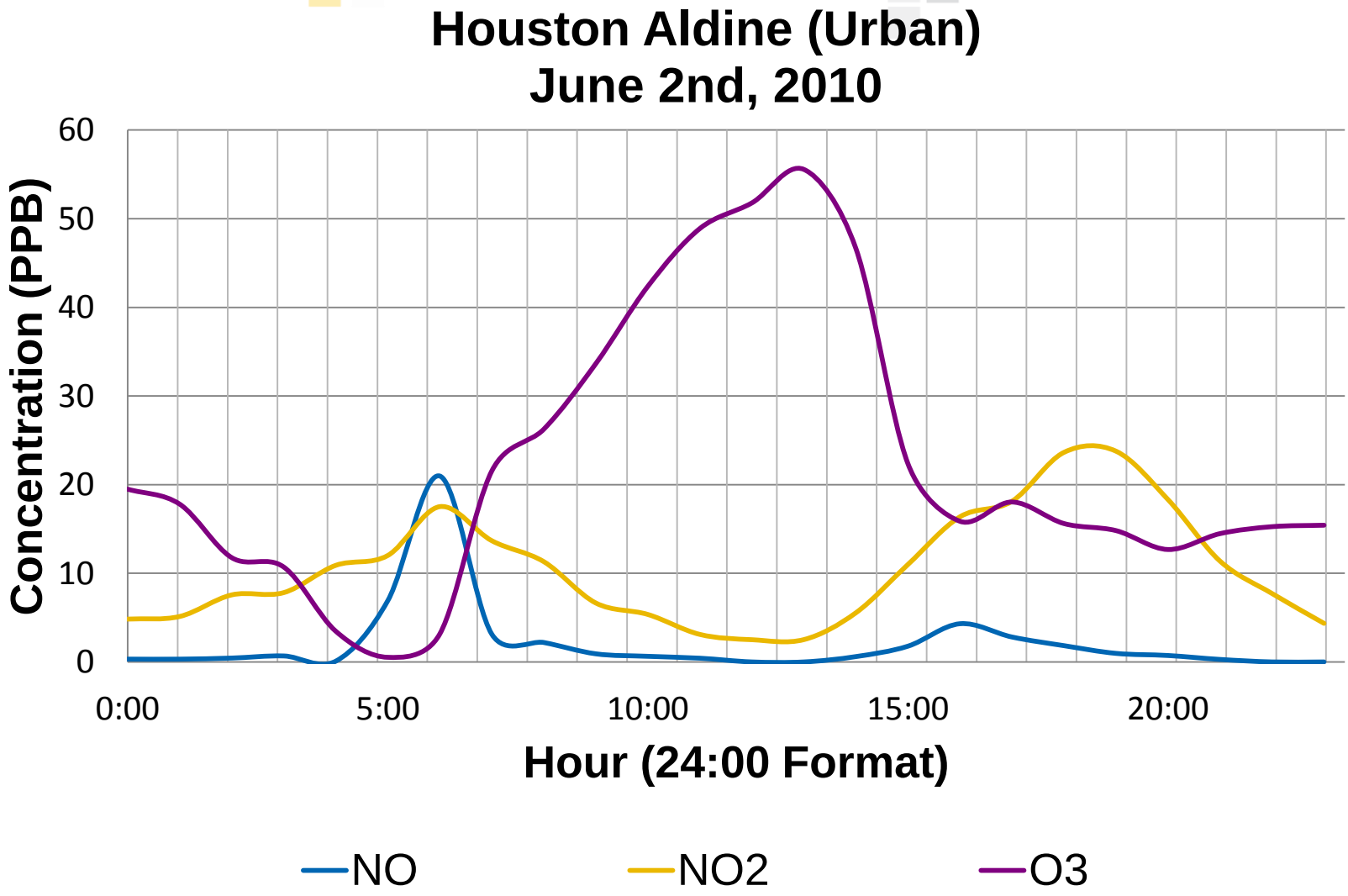
$$NO_2 \overset{h\nu}{\leftrightarrow} NO + O \quad \leftarrow \text{NO_2 Photolysis}$$

$$O + O_2 \leftrightarrow O_3 \quad \leftarrow \text{Ozone Formation}$$

$$O_3 + NO \leftrightarrow NO_2 + O_2 \quad \leftarrow \text{Titration}$$

- These reactions are balanced and cyclic and help to explain the changing diurnal patterns seen in ambient air quality data

Example Diurnal Pattern



NO_x Ambient Air Chemistry, cont'd

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> VOC's contribute significantly to ozone formation in the presence of sunlight

> During the day, titration is balanced by photolysis, resulting in lower levels of NO and NO_2

$$O_3 + NO \leftrightarrow NO_2 + O_2 \qquad NO_2 \overset{hv}{\leftrightarrow} NO + O$$

> Important Notes:

- NO, NO_2 and ozone ambient air ratios shift and change throughout the day
- There are *many* reactions taking place, not just titration or photolysis
- NO and NO_2 are also removed from the air during natural processes, mainly through formation of HNO_3 through direct absorption into ground, PM or cloud droplets

Additional NO_x Ambient Air Reactions[2]

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$$ROG + O + O_3 \leftrightarrow R\cdot + RCO + RO\cdot + OH\cdot$$

$$OH\cdot + NO_2 \leftrightarrow HNO_3$$

$$RO_2\cdot + NO \longrightarrow RO\cdot + NO_2$$

$$ROG + OH\cdot \longrightarrow R\cdot + H_2O$$
$$R\cdot + O \longrightarrow RO_2\cdot$$
$$RO_2\cdot + NO \longrightarrow RO\cdot + NO_2$$
$$RO\cdot + O_2 \longrightarrow HO_2\cdot + RCHO$$
$$HO_2\cdot + NO \longrightarrow NO_2 + OH\cdot$$

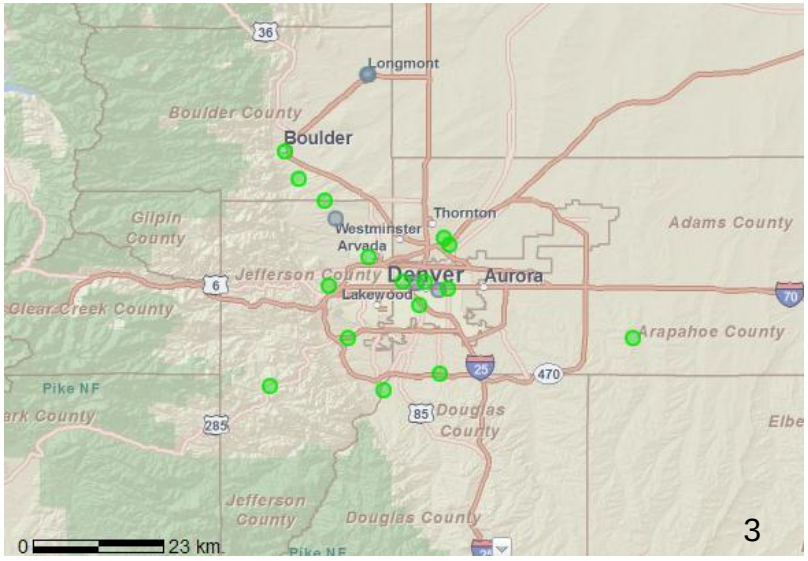
$$OH\cdot + CO \longrightarrow H + CO_2$$
$$H + O_2 \leftrightarrow HO_2\cdot$$
$$HO_2\cdot + NO \longrightarrow NO_2 + OH\cdot$$

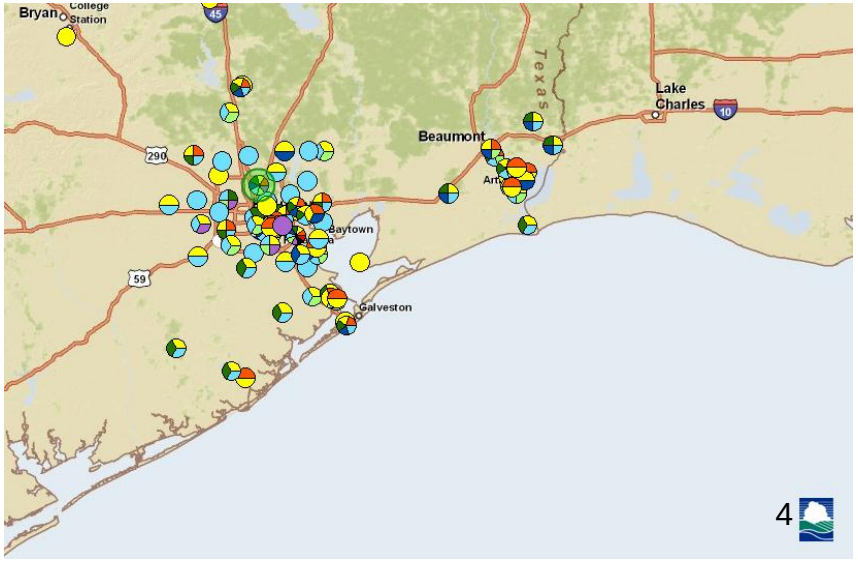
$$RO_2\cdot + NO_2 \longrightarrow ROONO_2$$

$$NO_2 + RC(=O)OO\cdot \longrightarrow RC(=O)OONO_2$$

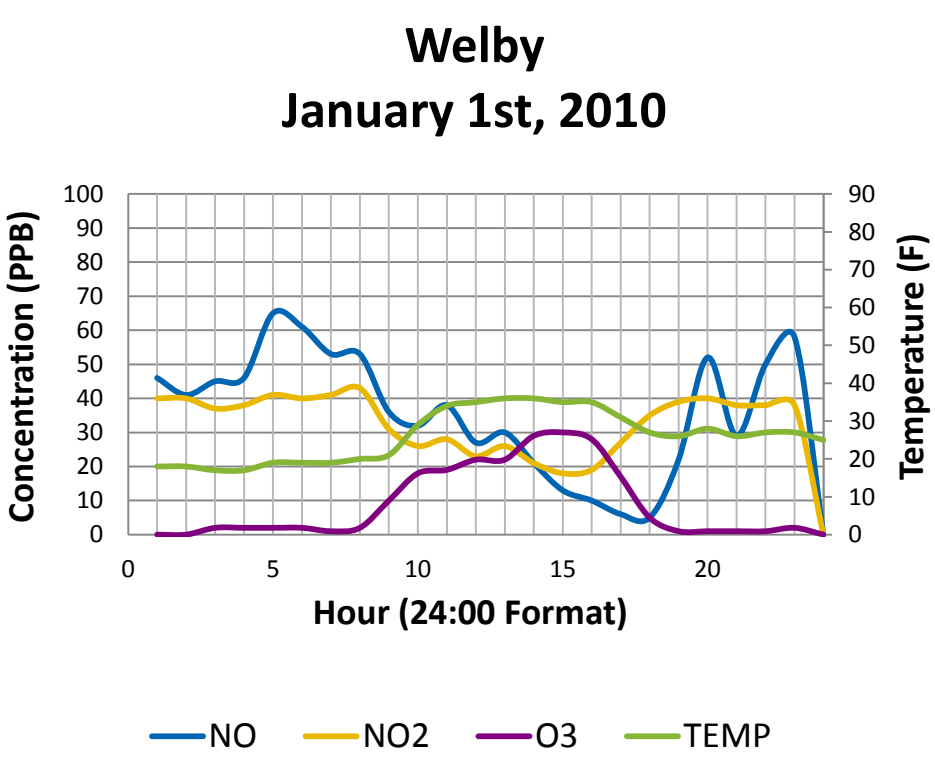
Ambient Air Quality Data Analysis

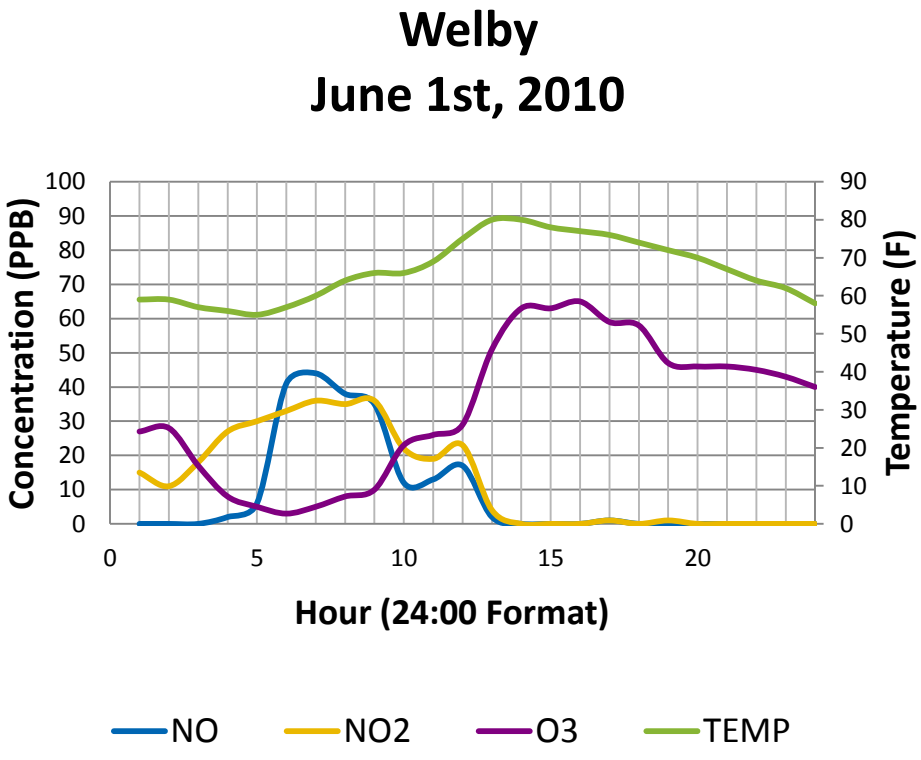
- Examination of NO/NO_2 ratios in natural ambient air
  - Denver, CO – Welby Ambient Monitoring Station
    - Seasonal Differences
  - Houston, TX – Houston Aldine and Lake Jackson Ambient Monitoring Stations
    - Urban vs. Rural Comparison





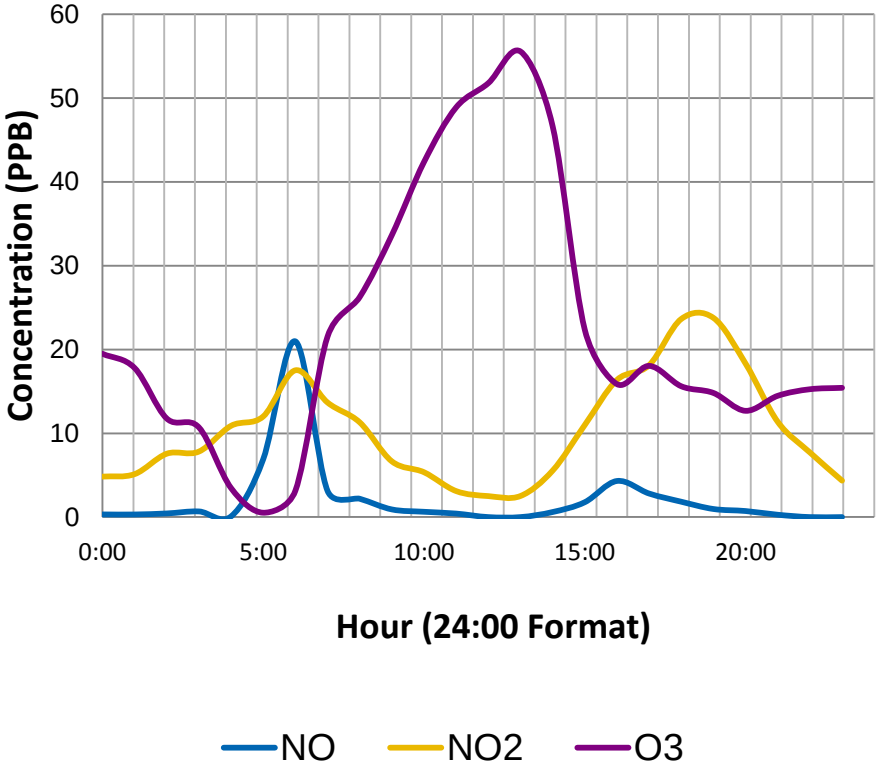
Denver Data – 2010



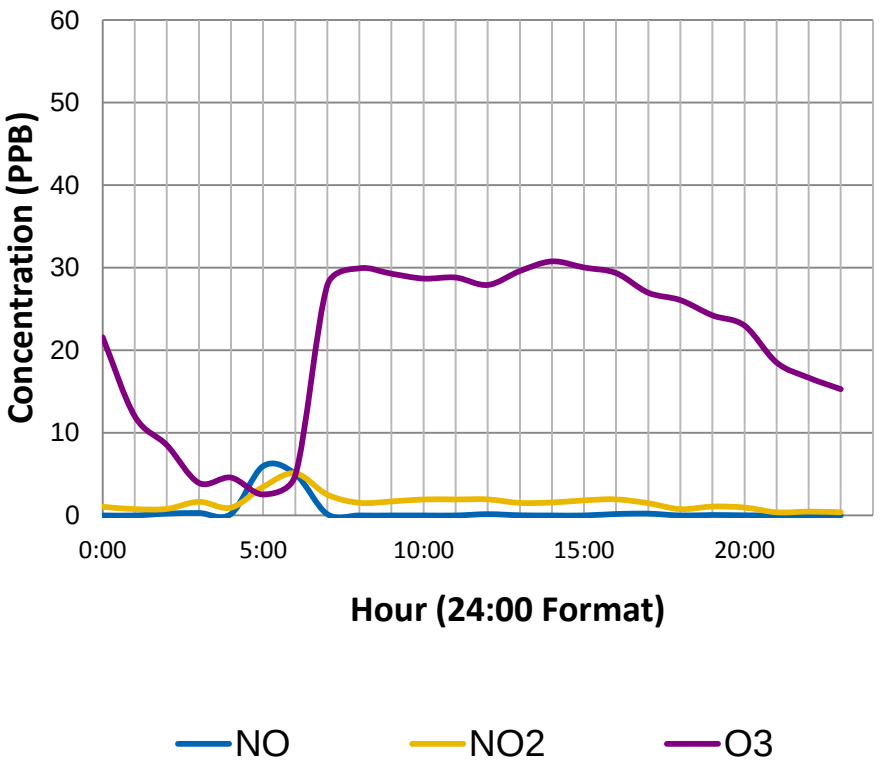


Urban vs. Rural Texas Data

Houston Aldine (Urban)
June 2nd, 2010

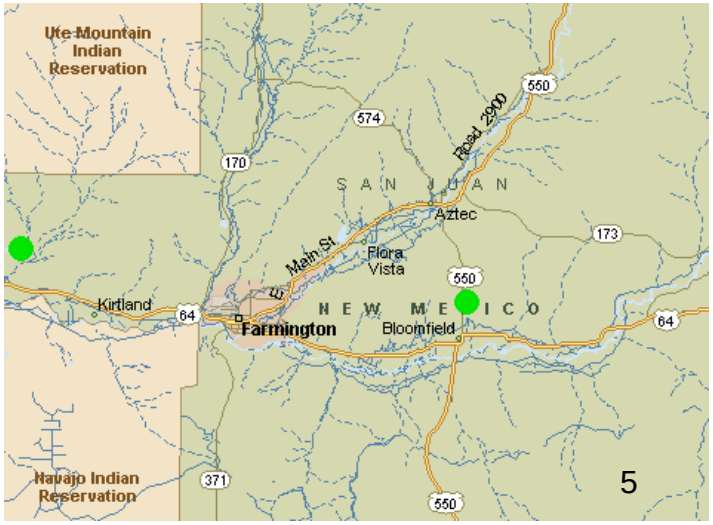


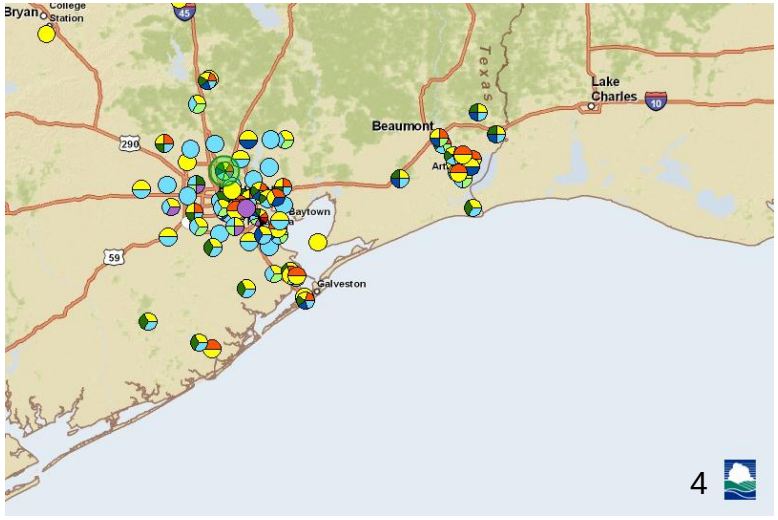
Lake Jackson (Rural)
June 2nd, 2010



Ambient NO_2/NO_x Ratios

- Reviewed actual NO_2/NO_x ratios seen in natural ambient air monitoring data
- Examined hourly data from three stations for NO_2/NO_x ratios
  - San Juan, New Mexico monitoring station (Jan 2010 – Dec 2010)
  - Bloomfield, New Mexico monitoring station (Mar 2010 – Jan 2011)
  - Houston Aldine, Texas monitoring station (Jan 2010 – Dec 2010)





Summary Table

	Maximum	Minimum	Average
NO_2/NO_x Ratios by Area, All Data			
San Juan, NM	1.00	0.10	0.78
Bloomfield, NM	1.00	0.16	0.73
Houston (Aldine), TX	1.00	0.00	0.84
Pollutant Concentration by Area			
NO_2 Concentration, ppb			
San Juan, NM	52	1	10.74
Bloomfield, NM	54	1	12.61
Houston (Aldine), TX	60.16	0	6.95
NO Concentration, ppb			
San Juan, NM	172	0	4.32
Bloomfield, NM	173	0	6.74
Houston (Aldine), TX	205.60	0	4.59
O_3 Concentration, ppb			
San Juan, NM	81	0	34.30
Bloomfield, NM	77	0	24.56
Houston (Aldine), TX	127.25	0	24.95

Data Points of Note

Location	Max Ratio	Max NO_2 ppb	Ratio	Max NO_2 ppb
San Juan	1.00	18	0.82	52
Bloomfield	1.00	24	0.63	54
Houston Aldine	1.00	24	0.91	60

- Data supports idea of different chemistry occurring in air
- Data supports that you can't apply a set ratio and have it be representative of what's actually happening
- There's even less conversion happening in a plume

NO_2/NO_x Ratio Observations

- Ambient air ratios of NO_2 and NO_x vary
  - Vary with time, concentration, and atmospheric conditions
  - Annual data set with great variations is not representative of short term data and hourly conditions
  - Average and median ratios of 0.75 reflect annual average air chemistry
  - Of note, we see *lower* ratios and less conversion when NO_2 is *higher* in concentration
  - Important because EPA is assuming that there's a high and uniform conversion
    - When examining the *highest* NO2 concentrations, you should be applying *lower* conversion ratios

Comparison of Ambient Ratios to NO/NO_2 Conversion

- High hourly conversion ratios (1.00) are *most conservative* but only seen when NO_x levels are very low, and hardly seen when NO_2 concentrations are above 20 ppb
- High annual conversion ratios (0.75-1.0) are also *conservative* but are only truly indicative of annual average ambient conditions
- Compliance model assumes one method of conversion; can't analyze additional reactions, including NO_2 removal processes
- Current assumed conversion ratios ignore complexity of local factors and chemistry
- No consistent ratio seen in ambient air quality data

Conclusion

- Hourly ambient air chemistry is incredibly complex and cannot be accurately accounted for with simplified models and assumptions
- Ambient air is well-mixed system in a quasi-equilibrium state where NOx chemistry is stable only over time
- Long-term ambient conditions and ratios are not representative of short-term plume concentrations and reactions

The purpose of the research was to raise questions regarding compliance with the new 1-hour NO_2 standard. If an intern who doesn't even have her college degree yet can find weaknesses and questionable assumptions, then maybe, just maybe*, there's something that needs to be further addressed.*

Thank you for your time!

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