Agriculture and Climate Change

AOSC 680

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Class Web Sites:
http://www2.atmos.umd.edu/~rjs/class/fall2024
https://umd.instructure.com/courses/1367293

Today, we'll begin with an overview of tropospheric ozone

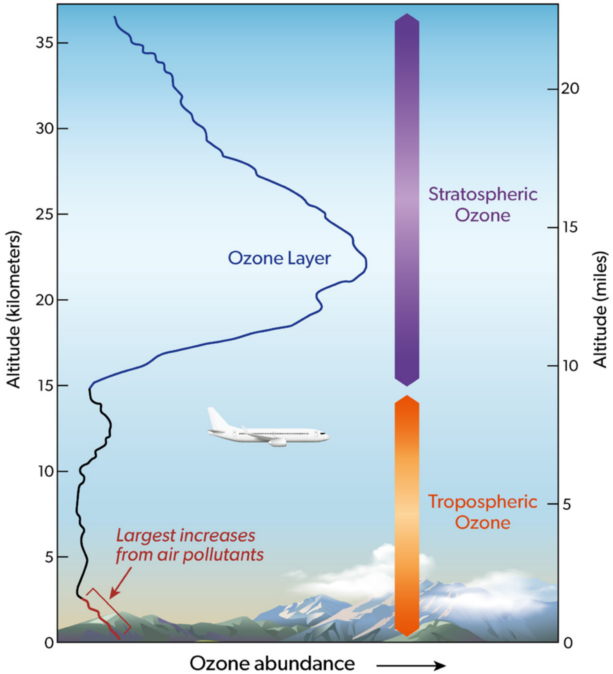

Fig Q1-2, WMO/UNEP 20 QAs Ozone

Lecture 21

14 November 2024

Tropospheric Ozone Production

$$OH + CO \rightarrow CO_2 + H$$

$$H + O_2 + M \rightarrow HO_2 + M$$

$$NO + HO_2 \rightarrow NO_2 + OH$$

$$NO_2 + h\nu \rightarrow NO + O$$

$$O + O_2 + M \rightarrow O_3 + M$$

Net: $$CO + 2\,O_2 \rightarrow CO_2 + O_3$$

Oxidation of CO in the presence of NO_x (NO & NO_2) leads to production of tropospheric O_3

Tropospheric Ozone Production

$$OH + \mathbf{CO} \rightarrow \mathbf{CO_2} + H$$

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$$NO_2 + h\nu \rightarrow NO + O$$

$$O + \mathbf{O_2} + M \rightarrow \mathbf{O_3} + M$$

$$\text{Net:} \quad \mathbf{CO + 2\ O_2 \rightarrow CO_2 + O_3}$$

NO & NO_2 : Emitted by fossil fuel combustion & biomass burning

$$N_2 + O_2 \xrightarrow{\text{High T}} 2\ NO$$

CO: Emitted by fossil fuel combustion & biomass burning

Complete combustion:

$$2\ C_8H_{18} + 25\ O_2 \rightarrow 16\ CO_2 + 18\ H_2O$$

Extreme, incomplete combustion:

$$2\ C_8H_{18} + 17\ O_2 \rightarrow 16\ CO + 18\ H_2O$$

OH & HO_2 , termed HOx: produced by the reaction of $O(^1D)$ with H_2O

Tropospheric Ozone Production

$$OH + \mathbf{CO} \rightarrow \mathbf{CO_2} + H$$

$$H + \mathbf{O_2} + M \rightarrow HO_2 + M$$

$$\mathbf{NO + HO_2 \rightarrow NO_2 + OH}$$

$$NO_2 + h\nu \rightarrow NO + O$$

$$O + \mathbf{O_2} + M \rightarrow \mathbf{O_3} + M$$

Net: $\mathbf{CO + 2\,O_2 \rightarrow CO_2 + O_3}$

Oxidation of CO in the presence of NO_x (NO & NO_2) leads to production of tropospheric O_3

Key chemical aspect **:**

NO converted to NO_2 without consumption of O_3

Tropospheric Ozone Production

***Suppose* NO *is converted to* NO$_2$ *by reaction with* O$_3$:**

$$OH + CO \rightarrow CO_2 + H$$

$$H + O_2 + M \rightarrow HO_2 + M$$

$$\mathbf{NO + O_3 \rightarrow NO_2 + O_2}$$

$$NO_2 + h\nu \rightarrow NO + O$$

$$O + O_2 + M \rightarrow O_3 + M$$

Net: **????????** → **????????**

Tropospheric Ozone Production

***Suppose* NO *is converted to* NO_2 *by reaction with* O_3 :**

$$OH + CO \rightarrow CO_2 + H$$

$$H + O_2 + M \rightarrow HO_2 + M$$

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$NO_2 + h\nu \rightarrow NO + O$$

$$O + O_2 + M \rightarrow O_3 + M$$

Net: $CO + O_2 + OH \rightarrow CO_2 + HO_2$

No ozone production!

Tropospheric Ozone Production

Suppose NO *is converted to* NO_2 *by reaction with* O_3 :

$$OH + CO \rightarrow CO_2 + H$$

$$H + O_2 + M \rightarrow HO_2 + M$$

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$NO_2 + h\nu \rightarrow NO + O$$

$$O + O_2 + M \rightarrow O_3 + M$$

$$\text{Net: } CO + O_2 + OH \rightarrow CO_2 + HO_2$$

Next key question: ????????

Tropospheric Ozone Production

Suppose NO *is converted to* NO_2 *by reaction with* O_3 **:**

$$\mathbf{OH} + \mathbf{CO} \rightarrow \mathbf{CO_2} + H$$

$$H + O_2 + M \rightarrow \mathbf{HO_2} + M$$

$$\mathbf{NO} + \mathbf{O_3} \rightarrow \mathbf{NO_2} + \mathbf{O_2}$$

$$NO_2 + h\nu \rightarrow NO + O$$

$$O + \mathbf{O_2} + M \rightarrow O_3 + M$$

$$\text{Net: } \mathbf{CO} + \mathbf{O_2} + \mathbf{OH} \rightarrow \mathbf{CO_2} + \mathbf{HO_2}$$

Next key question: how does HO_2 go back to OH ?

Tropospheric Ozone Production

***Suppose* NO *is converted to* NO_2 *by reaction with* O_3 :**

$$OH + CO \rightarrow CO_2 + H$$

$$H + O_2 + M \rightarrow HO_2 + M$$

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$NO_2 + h\nu \rightarrow NO + O$$

$$O + O_2 + M \rightarrow O_3 + M$$

~~Net: $CO + O_2 + OH \rightarrow CO_2 + HO_2$~~

$$HO_2 + O_3 \rightarrow OH + 2\ O_2$$

Net: $$CO + O_3 \rightarrow CO_2 + O_2$$

Tropospheric Ozone Production

Suppose NO is converted to NO_2 by reaction with O_3 :

$$OH + CO \rightarrow CO_2 + H$$

$$H + O_2 + M \rightarrow HO_2 + M$$

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$NO_2 + h\nu \rightarrow NO + O$$

$$O + O_2 + M \rightarrow O_3 + M$$

~~Net: $CO + O_2 + OH \rightarrow CO_2 + HO_2$~~

$$HO_2 + O_3 \rightarrow OH + 2\ O_2$$

$$\text{Net: } CO + O_3 \rightarrow CO_2 + O_2$$

Have now consumed O_3 because it is used to convert NO to NO_2 and HO_2 to OH !

Tropospheric Ozone Production

$$OH + \mathbf{CO} \rightarrow \mathbf{CO_2} + H$$

$$H + \mathbf{O_2} + M \rightarrow HO_2 + M$$

$$\mathbf{HO_2 + NO \rightarrow OH + NO_2}$$

$$NO_2 + h\nu \rightarrow NO + O$$

$$O + \mathbf{O_2} + M \rightarrow \mathbf{O_3} + M$$

$$\text{Net:} \quad \mathbf{CO} + \mathbf{2\,O_2} \rightarrow \mathbf{CO_2} + \mathbf{O_3}$$

Chain Mechanism for production of ozone

Chemical Initiation: H_2O+O(^{1}D) $\rightarrow$ 2OH & human emission of NO, CO

Since method for conversion of NO to NO_2 is *crucial* for whether O_3 is produced by this chain mechanism, chemists consider production of tropospheric ozone to be "limited" by k[HO_2][NO]

Tropospheric Ozone Production

$$
\begin{aligned}
CO + OH &\rightarrow CO_2 + H \\
H + O_2 + M &\rightarrow HO_2 + M \\
HO_2 + NO &\rightarrow OH + NO_2 \\
NO_2 + h\nu &\rightarrow NO + O \\
O + O_2 + M &\rightarrow O_3 + M
\end{aligned}
$$

$$\text{Net:} \quad CO + 2\,O_2 \rightarrow CO_2 + O_3$$

$$
\begin{aligned}
RH + OH &\rightarrow R + H_2O \\
R + O_2 + M &\rightarrow RO_2 + M \\
RO_2 + NO &\rightarrow RO + NO_2 \\
RO + O_2 &\rightarrow HO_2 + R'CHO \\
HO_2 + NO &\rightarrow OH + NO_2 \\
2 \times \quad NO_2 + h\nu &\rightarrow NO + O \\
2 \times \quad O + O_2 + M &\rightarrow O_3 + M
\end{aligned}
$$

$$\text{Net:} \quad RH + 4O_2 \rightarrow R'CHO + H_2O + 2\,O_3$$

VOC: Volatile Organic Compounds

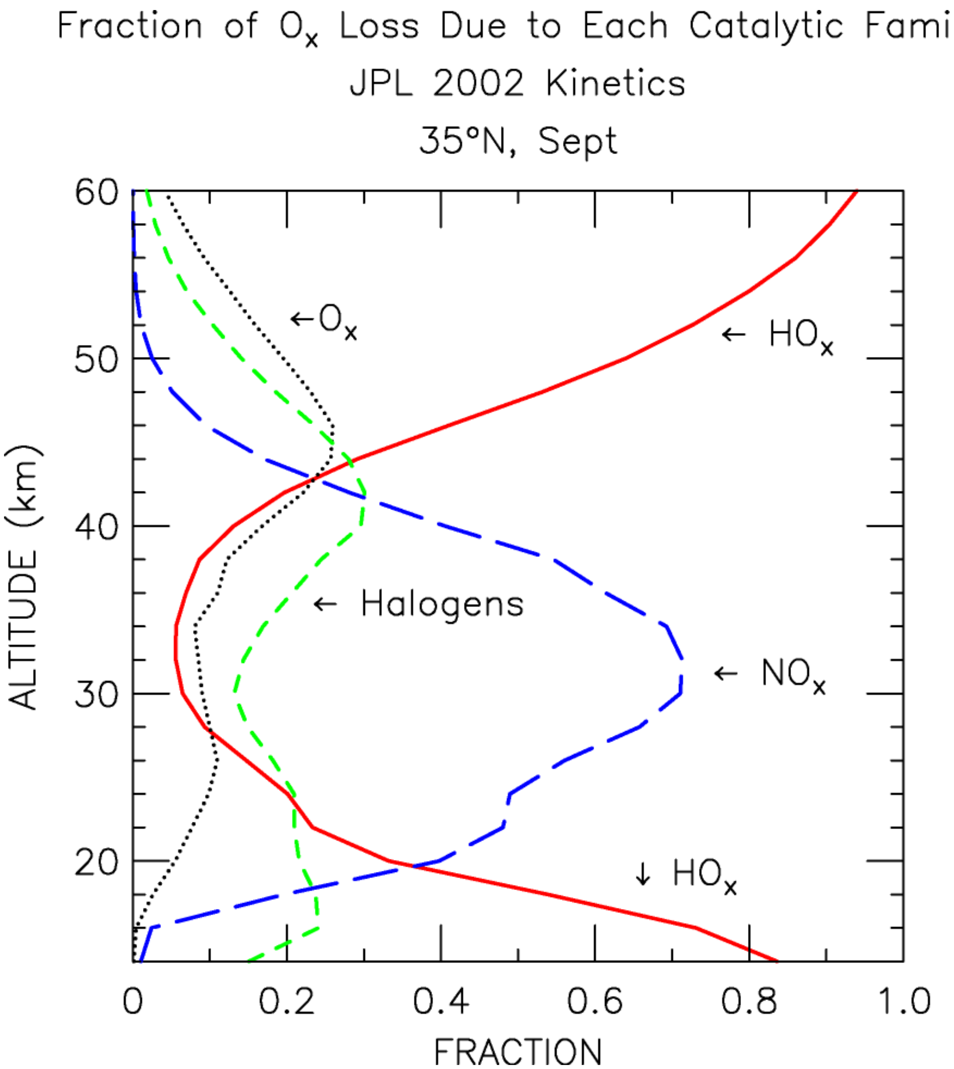
Produced by trees, fossil fuel vapor, and non-controlled auto emissions

Strong source of HO_x (OH & HO_2) & O_3 (depending on NO_x levels)

Examples of RH and R'CHO : **CH_4 (methane) → CH_2O (formaldehyde)**
: C_2H_6 (ethane) → CH_3CHO (acetaledhyde)
: C_3H_8 (propane) → CH_3COCH_3 (acetone)

Ozone Production "limited" by $k[HO_2][NO] + \Sigma\, k_i\, [RO_2]_i\, [NO]$

Stratospheric Photochemistry: Odd Oxygen Loss By Families



Calculated fraction of odd oxygen loss due to various families of radicals

After Osterman et al., GRL, 24, 1107, 1997;
Sen et al., JGR, 103, 3571, 1998;
Sen et al., JGR, 104, 26653, 1999.

One Atmosphere – One Photochemistry

Stratosphere

HO$_2$ formation:

$$OH + O_3 \rightarrow HO_2 + O_2$$

HO$_2$ loss:

$$HO_2 + O_3 \rightarrow OH + 2\ O_2$$

Net: $$O_3 + O_3 \rightarrow 3\ O_2$$

Rate HO$_2$ Formation = k_{OH+O3}×[OH][O$_3$] + k_{OH+CO}×[OH][CO]

Rate HO$_2$ Loss = k_{HO2+O3}×[HO$_2$][O$_3$] + k_{HO2+NO}×[HO$_2$][NO]

Troposphere

HO$_2$ formation:

$$OH + CO \xrightarrow{O_2} HO_2 + CO_2$$

HO$_2$ loss:

$$HO_2 + NO \rightarrow OH + NO_2$$

Followed by:

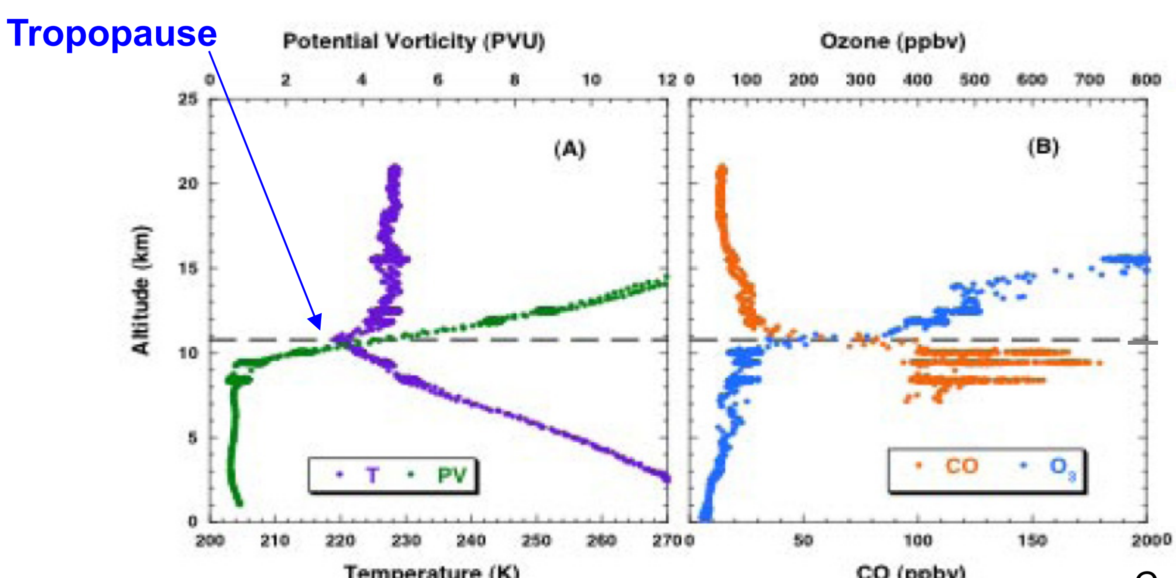
$$NO_2 + h\nu \rightarrow NO + O$$

$$O + O_2 + M \rightarrow O_3 + M$$

Net: $$CO + 2\ O_2 \rightarrow CO_2 + O_3$$

Rate HO$_2$ Formation = k_{OH+O3}×[OH][O$_3$] + **k_{OH+CO}×[OH][CO]**

Rate HO$_2$ Loss = k_{HO2+O3}×[HO$_2$][O$_3$] + **k_{HO2+NO}×[HO$_2$][NO]**

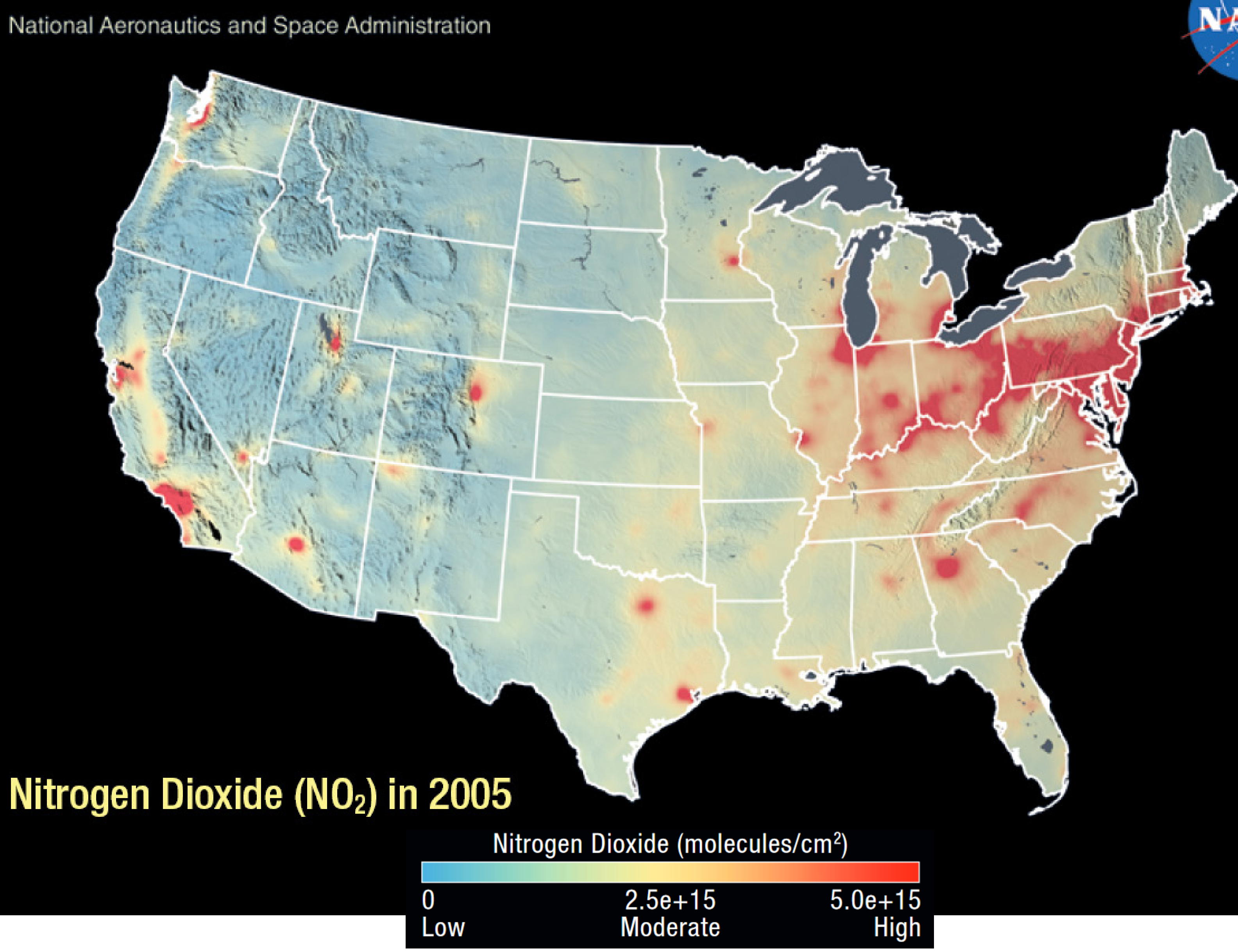


Above Tropopause:
Lots of O$_3$, little CO & NO

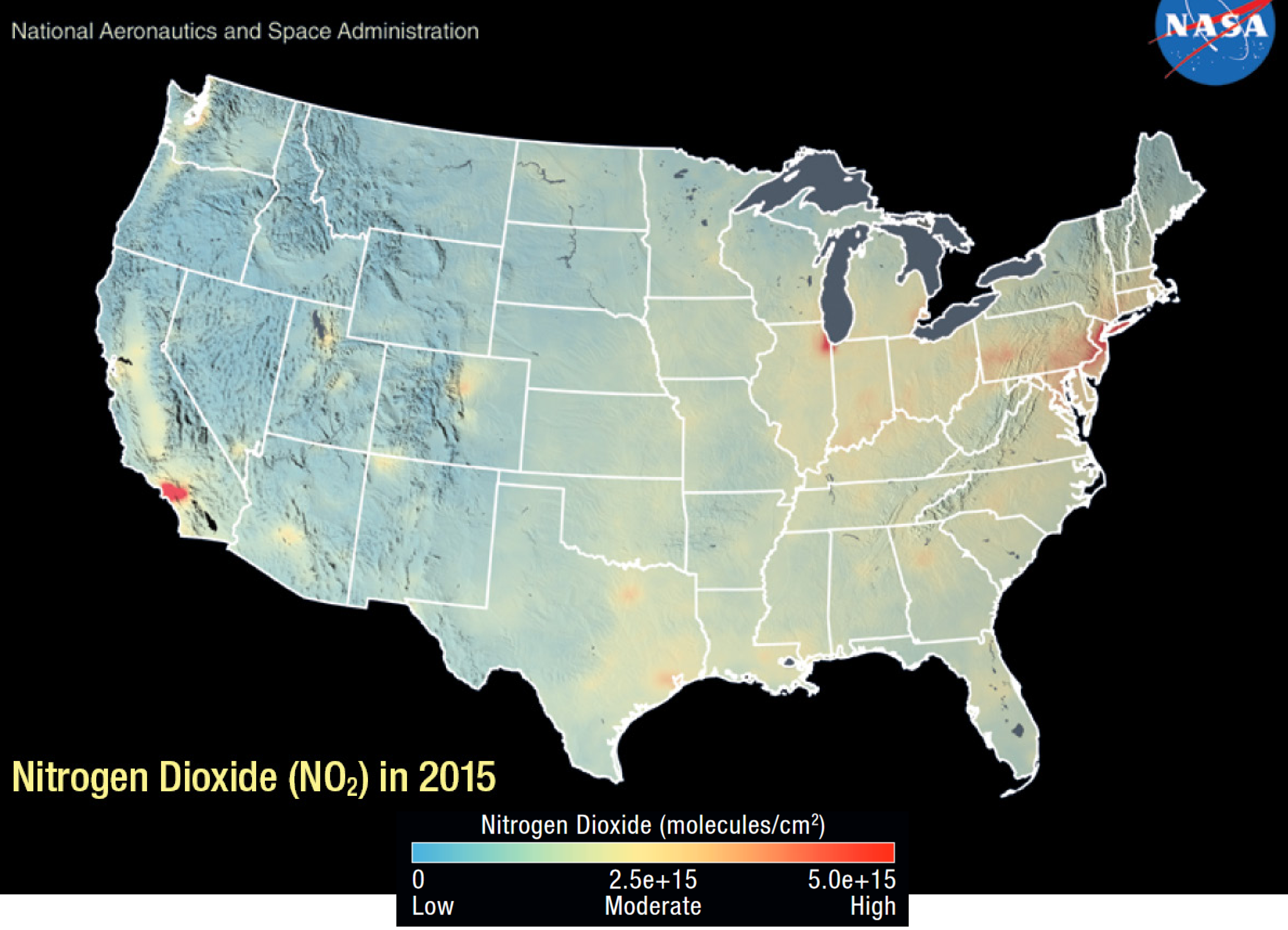
Below Tropopause:
Lots of CO & NO, little O$_3$

Courtesy of Laura Pan, NCAR

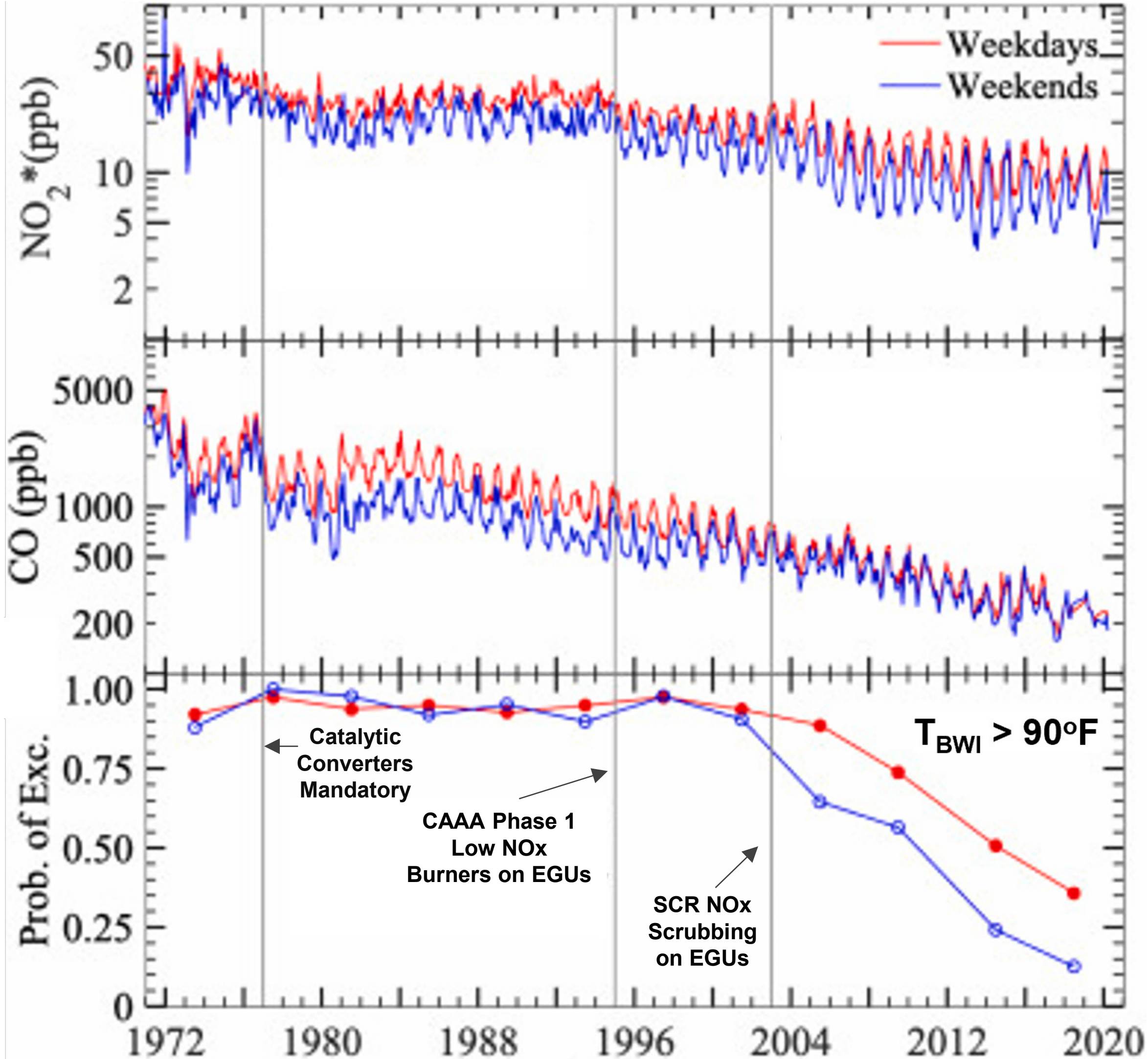
US Trends: NO_2



US Trends: NO_2

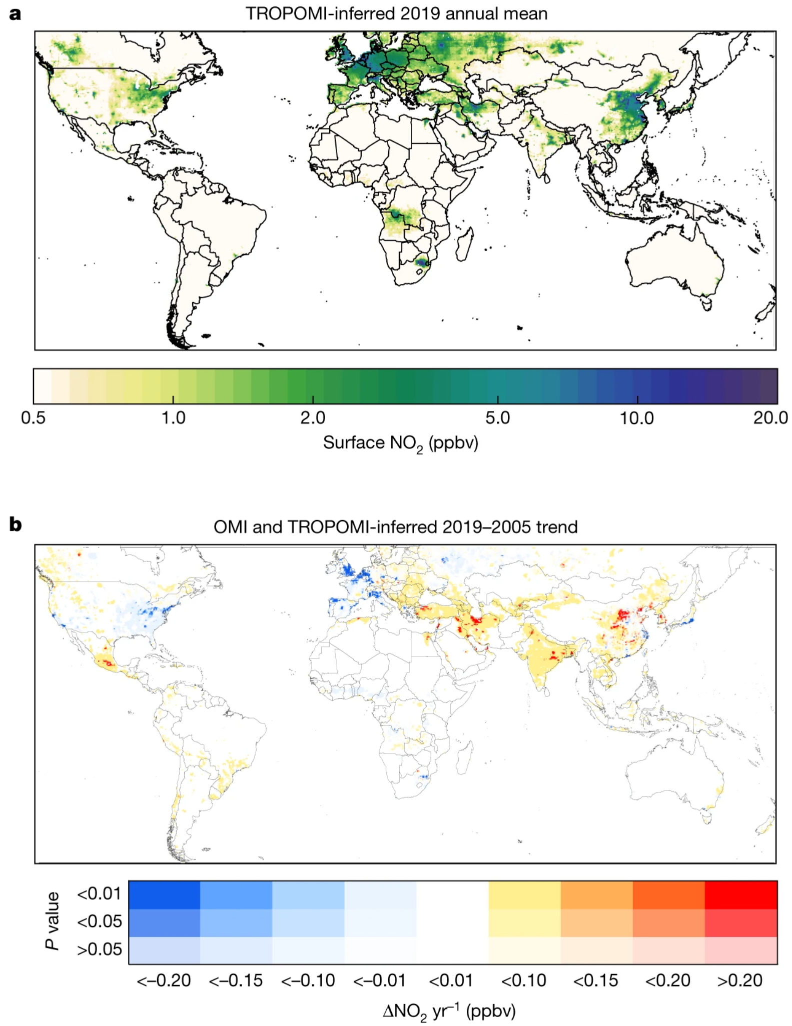


Probability of Surface O_3 Exceedance: DC, MD, and Northern VA



CAAA: Clean Air Act Amendment
EGU: Electrical Generating Units (aka Power Plants)
SCR: Selective Catalytic Reduction

Roberts et al., *Atmos. Envir.*, 2022
https://www.sciencedirect.com/science/article/pii/S1352231022003041



Top: Space-borne measurement of NO_2 in lower troposphere, 2019
Bottom: 15 year trend in NO_2
Observations from the NASA OMI & European TropOMI instruments

Cooper *et al.*, *Nature*, 2022
https://www.nature.com/articles/s41586-021-04229-0

Effect of surface ozone on crop production is a major research topic

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crop production ozone

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Surface **ozone** impacts on major **crop production** in China from 2010 to 2017
D Li, D Shindell, D Ding, X Lu, L Zhang... - ... Chemistry and Physics, 2022 - acp.copernicus.org
... to study the long-term trend of **ozone**-induced **crop production** losses from 2010 to 2017 in China. We find that overall the **ozone**-induced **crop production** loss in China is significant and ...
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Ozone pollution threatens the **production** of major staple **crops** in East Asia
Z Feng, Y Xu, K Kobayashi, L Dai, T Zhang... - Nature Food, 2022 - nature.com
... surface O 3 levels to **crop production** in East Asia, ... to **crop production** because 60% of China's wheat harvest comes from the provinces in the North China Plain 30 . A glance at **crop** ...
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[HTML] Reductions in **crop** yields across China from elevated **ozone**
Y Wang, O Wild, K Ashworth, X Chen, Q Wu, Y Qi... - Environmental ..., 2022 - Elsevier
... related to both elevated **ozone** during the growing season, and to **crop production** intensity. ... have high **crop production** loss. In conclusion, the total **production** loss for all **crops** is ...
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Approaches to investigate **crop** responses to **ozone** pollution: from O_3-FACE to satellite-enabled modeling
CM Montes, HJ Demler, S Li, DG Martin... - The Plant ..., 2022 - Wiley Online Library
... (c) The fraction of total harvested area in hectares (ha) comprising C 4 **crop production** in each country, obtained from 2010–2019 average global **crop production** data from the Food ...
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