Tropospheric Ozone and Air Quality
AOSC / CHEM 433 & AOSC / CHEM 633

Ross Salawitch

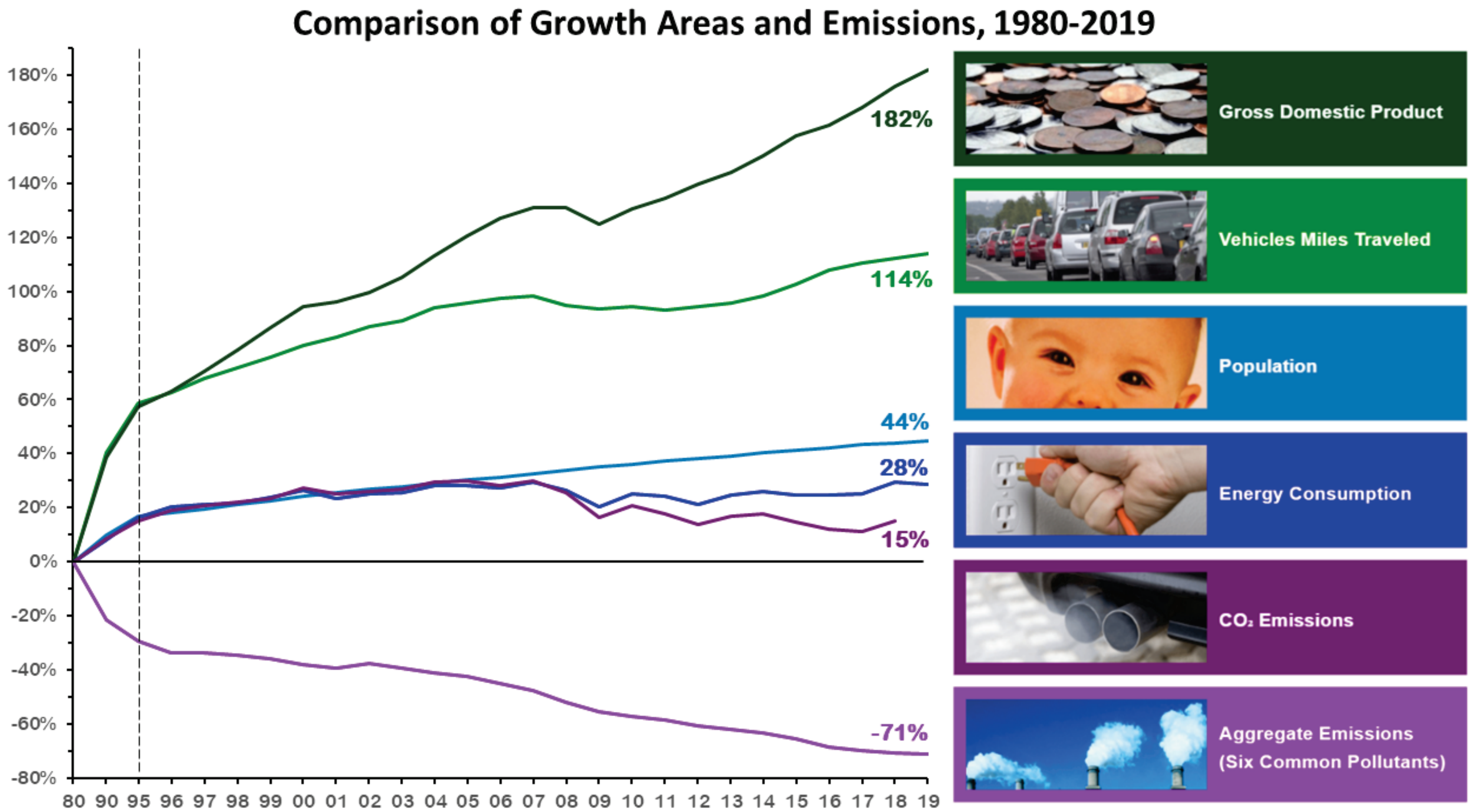
Class Web Sites:
http://www2.atmos.umd.edu/~rjs/class/fall2020
https://myelms.umd.edu/courses/1291919

Today:
- **Tropospheric ozone production mechanism (CO, NO_x, and VOCs)**
- **Recent improvements of air quality**
- **Coupling of meteorology, and perhaps climate change, to air quality**

Lecture 13 Catch-Up

28 October 2020

Significant Improvements in U.S. Air Quality, Past Four Decades



https://www.epa.gov/air-trends/air-quality-national-summary#air-quality-trends

U.S. EPA Six Criteria Pollutants: CO, ground-level O_3, particulate matter (PM), NO_2, SO_2, and lead
https://www.epa.gov/sites/production/files/2015-10/documents/ace3_criteria_air_pollutants.pdf

Tropospheric Ozone Production

$$CO + OH \rightarrow CO_2 + H$$
$$H + O_2 + M \rightarrow HO_2 + M$$
$$HO_2 + NO \rightarrow OH + NO_2$$
$$NO_2 + h\nu \rightarrow NO + O$$
$$O + O_2 + M \rightarrow O_3 + M$$

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

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

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

Chain Mechanism for production of ozone

Chemical Initiation: Human emission of NO, CO and either human (RO_2) or natural (HO_2) hydrogen radicals

Ozone production: k[HO_2][NO]

Termination: can occur via either:

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$

or

$$OH + NO_2 + M \rightarrow HNO_3 + M$$

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High NO_x ($NO+NO_2$) forces termination via this route!

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As NO rises, $[HO_2]/[OH]$ ratio falls (HO_2 titrated to OH)

As NO_x rises, $[HO_2]$ falls faster than [NO] rises

⇨ What will happen to production of O_3 ?

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Prod of $HO_2 \approx k_1[CO][OH]$ because $H+O_2+M$ is near immediate

For high NOx:

Loss of $HO_2 \approx k_3[HO_2][NO]$

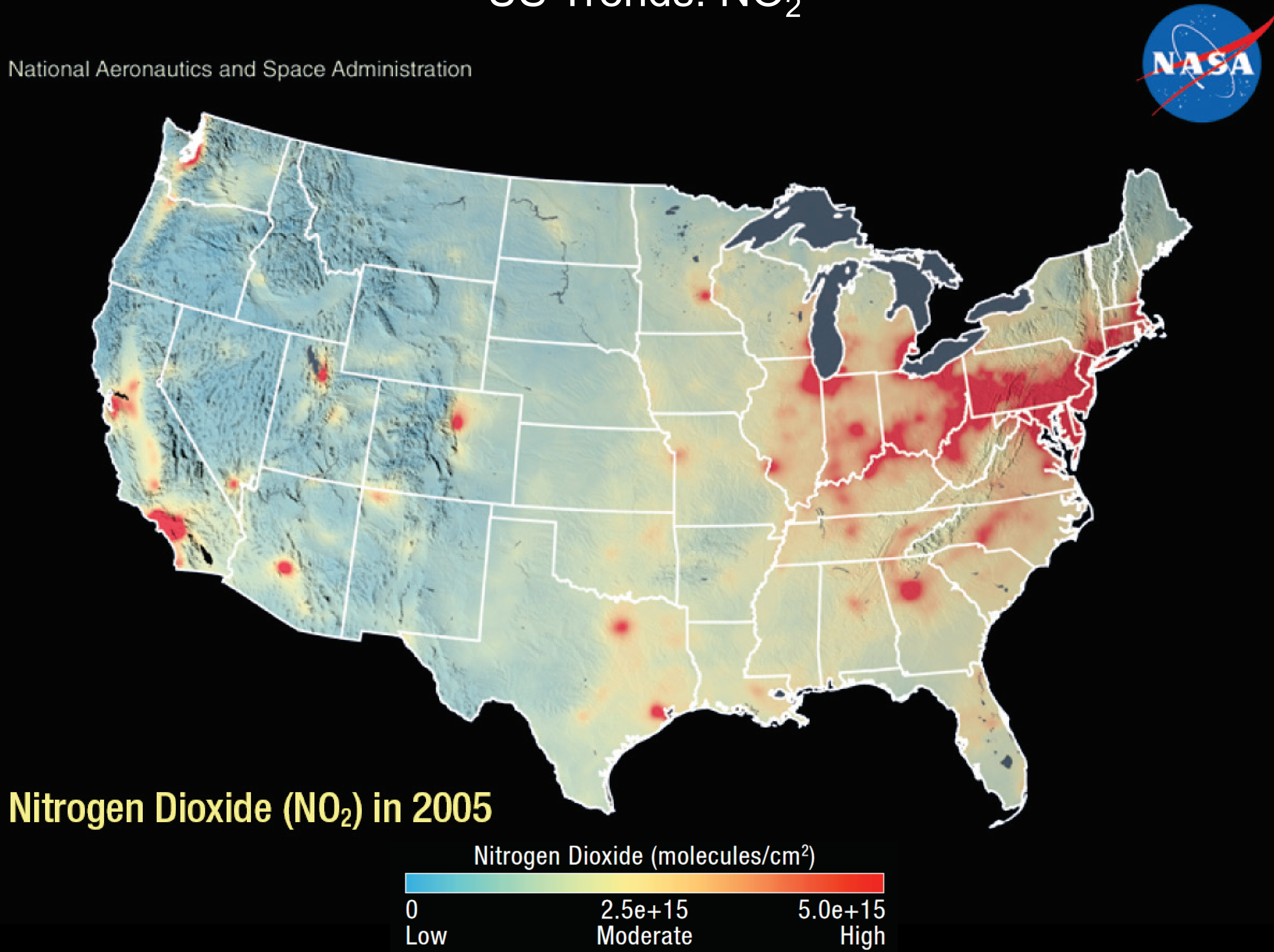
Therefore if Prod of HO_2=Loss of HO_2,

$$[HO_2]/[OH] \approx k_1[CO] / k_3[NO]$$

However, Prod of HO_x ($OH+HO_2$) limited by rate of $O(^1D)+H_2O$

If Loss of HO_x is also controlled by NO_2, then $[HO_2]$ will fall faster than [NO] rises.

US Trends: NO_2



https://aura.gsfc.nasa.gov/images/outreach/NO2_2005-15_final.pdf

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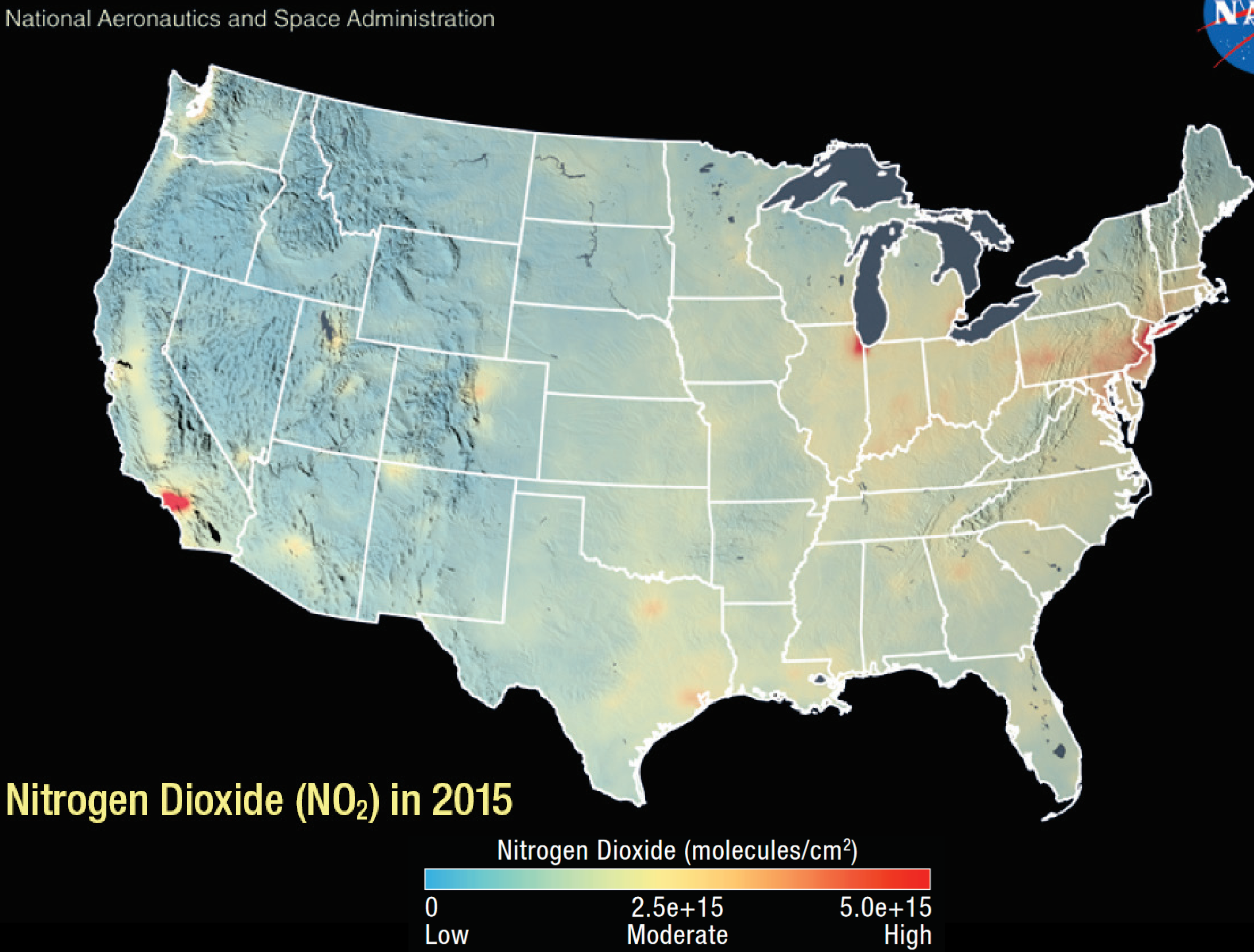

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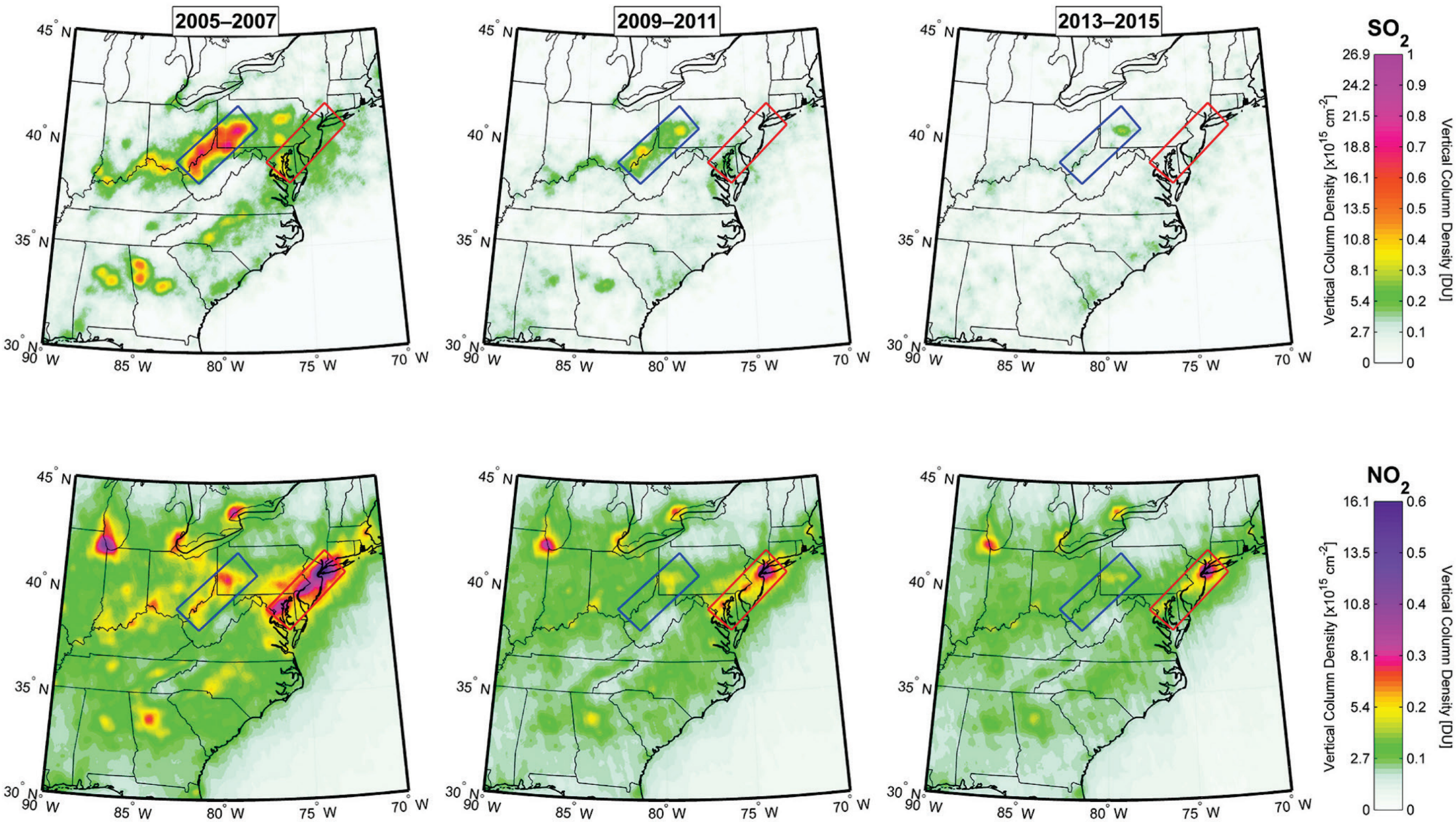
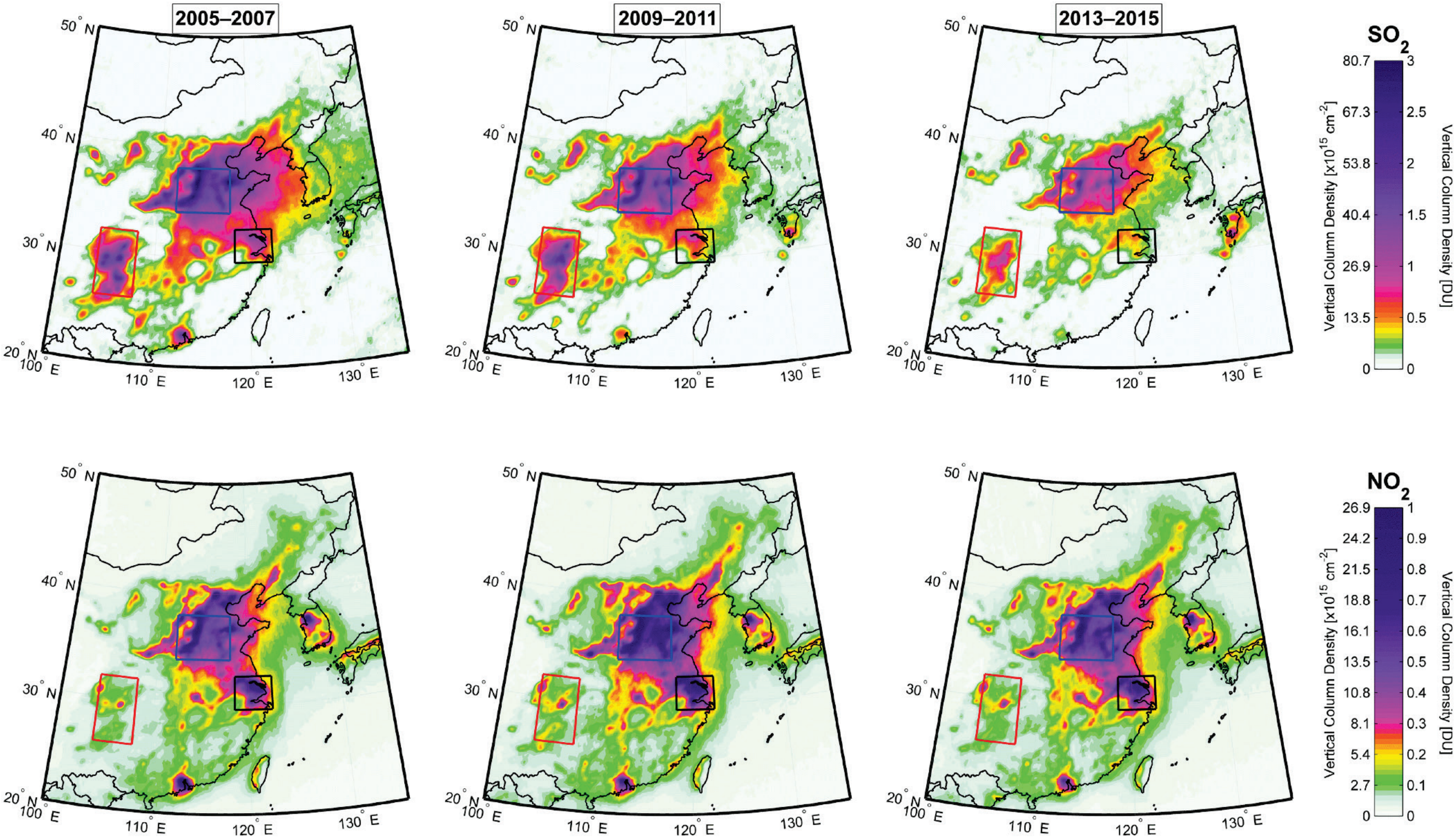
US Trends: NO_2 and SO_2



Krotkov *et al*., *ACP*, 2016

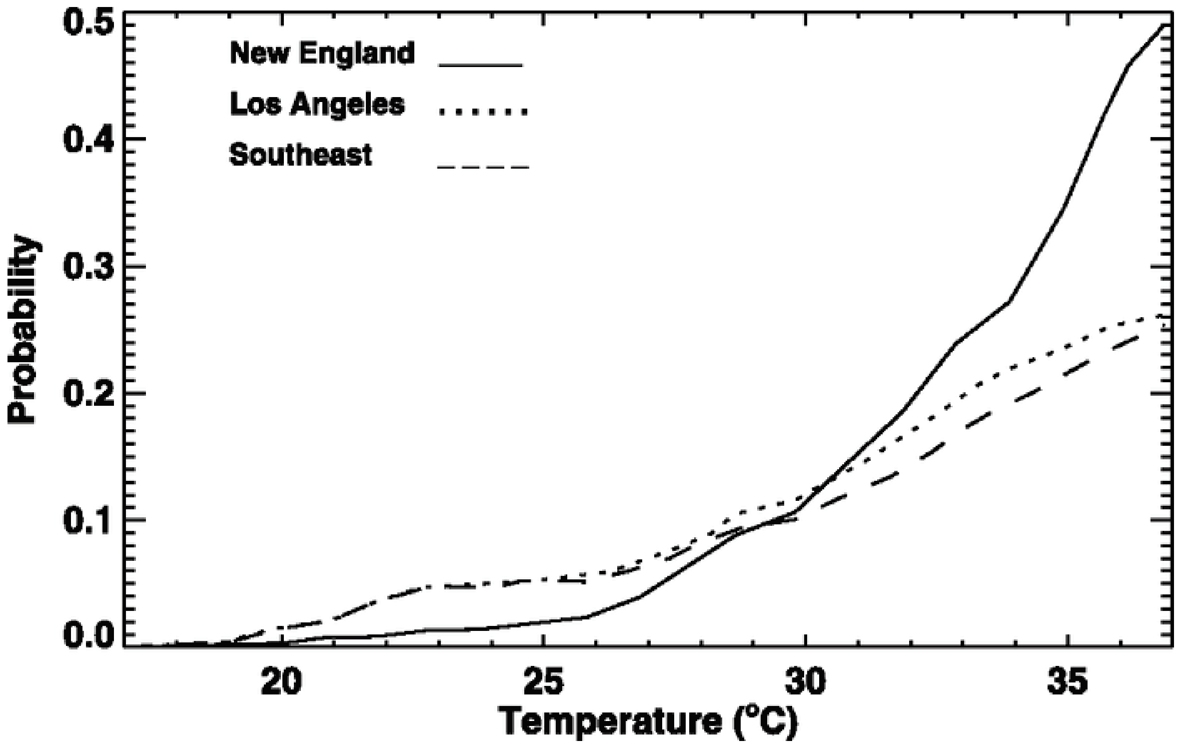
China Trends: NO_2 and SO_2



Krotkov *et al.*, *ACP*, 2016

Day-to-day meteorology (weather!) affects severity and duration of pollution episodes

Probability of ozone exceedance vs. daily max. temperature

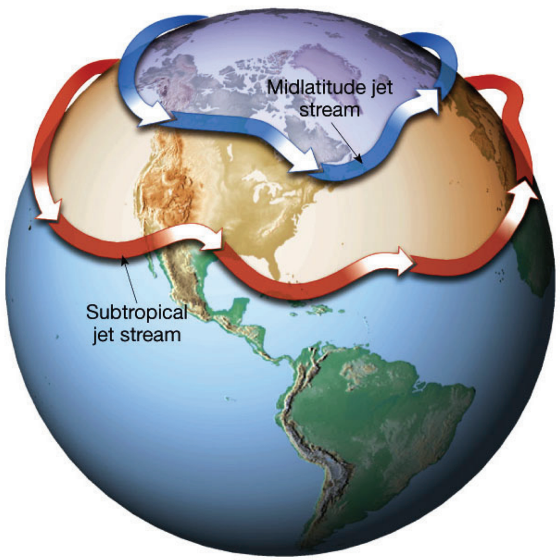


Lin et al. 2001

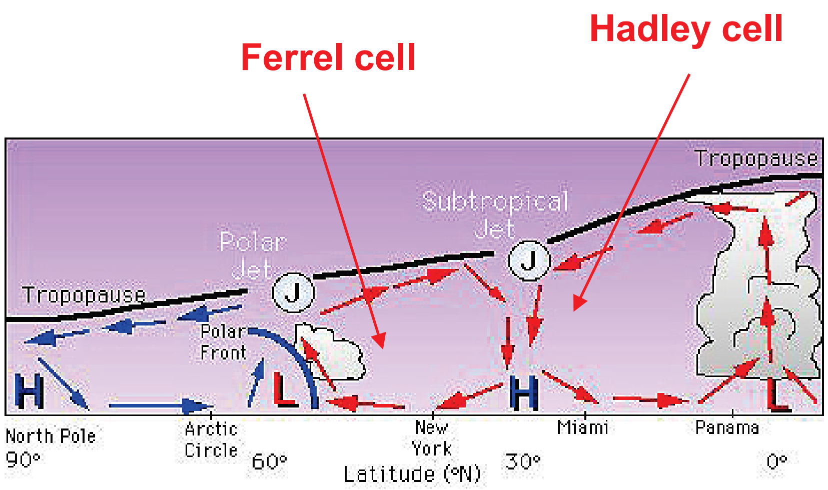
Why does probability of high ozone rise with increasing temperature?

Faster chemical reactions, increased anthropogenic emission (NO_x), increased biogenic emission (mainly isoprene, C_5H_8), and *stagnation of air*.

Subtropical Jet



http://www.ux1.eiu.edu/~cfjps/1400/FIG07_014A.jpg



http://www.fas.org/irp/imint/docs/rst/Sect14/jet_stream.jpg

Subtropical Jet: area where poleward descending branch of the Hadley Circulation meets the equatorward descending of the Ferrel Cell (see Lecture 3)

Semi-permanent area of high pressure, fair weather, low rainfall:
conditions conductive to high ozone

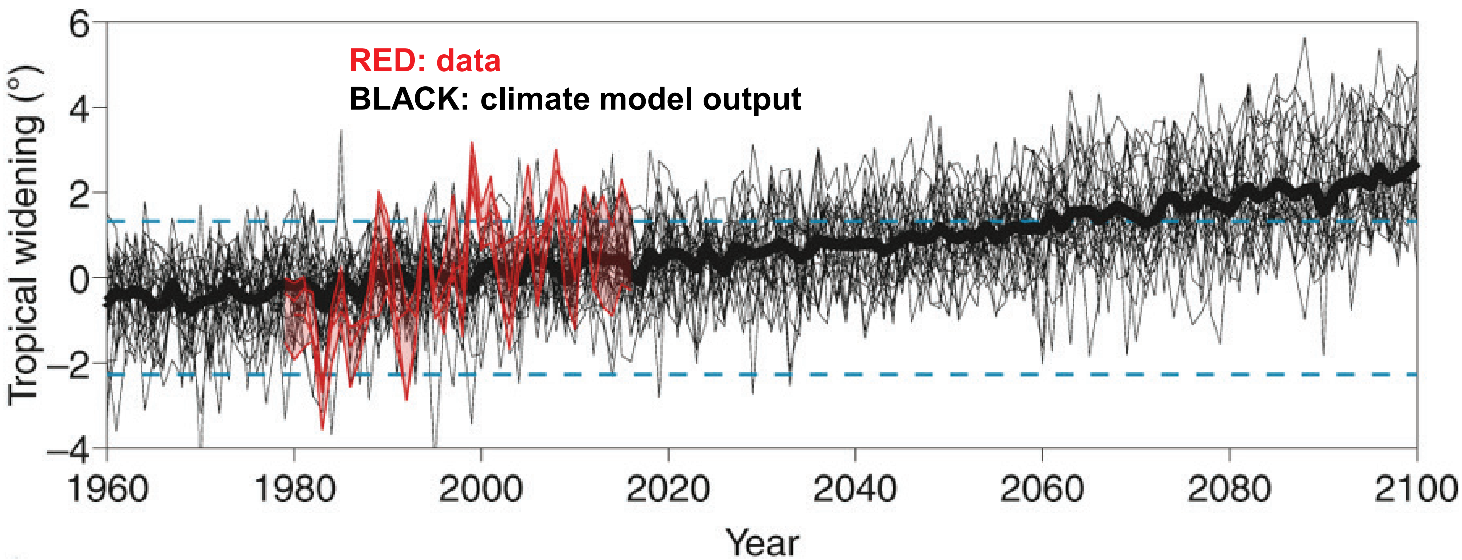
Climate Change and Air Pollution

Poleward expansion of the sub-tropical jet:

- Surface ozone highs occur along Subtropical Jet
- Driving forces:

  a) rising levels of GHGs lead to a weakening of the equator to pole due to more rapid warming at extra-tropical latitudes compared to tropics;

  b) prior increases in CFCs lead to ozone depletion in the extra-tropics, which exacerbates stratospheric cooling



Staten *et al*., Nature Climate Change, 2018
https://www.nature.com/articles/s41558-018-0246-2/

- **Computer models predict increase in severity and duration of pollution episodes over Midwest , Mid-Atlantic, and Northeast U.S. in 2050, even for constant emissions**