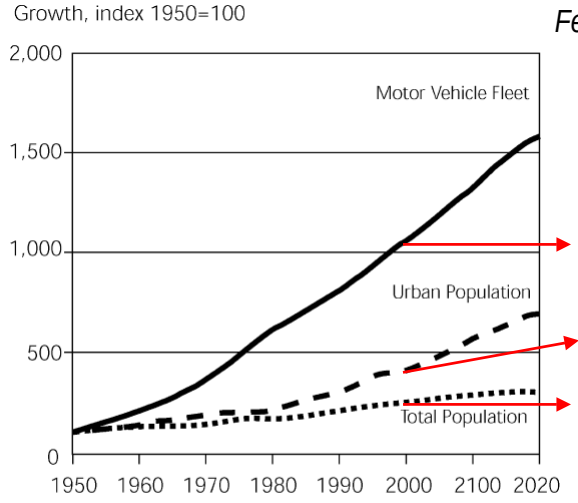
Air pollution

Increases since 1950 in world population, urban population and number of motor vehicles

Fenger, Atmos. Env., 33 (1999).



Numbers for year 2000:

~ 600 millions vehicles

~ 44% of total pop. (75% in develp. Countries)

~ 6 billions

Fig. 1. The increase since 1950 of the total world population, the urban population and the number of motor vehicles – excluding motorbikes and three wheelers (UNEP/WHO, 1992).

U. S. Air Pollution Laws

Air Pollution Control Act of 1955

Clean Air Act of 1963 (smokestack emission regulations only)

Motor Vehicle Air Pollution Control Act of 1965 (HCs and CO emissions from vehicles)

Air Quality Act of 1967

Clear Air Act Amendments of 1970

- U. S. Environmental Protection Agency (EPA)
- National Ambient Air Quality Standards (NAAQS); Criteria Air Pollutants; Attainment/nonattainment areas
- New Source Performance Standards (NSPS)
- National Emission Standards for Hazardous Pollutants (asbestos, mercury, arsenic…)
- Congressional control of automobile emissions

Clear Air Act Amendments of 1977+ 1990

Clear Air Act Revision of 1997

- Change in ozone standards
- Addition of $PM_{2.5}$ standard

Acid Rain program (1995)

NOx budget Program (1999)

Clean Air Interstate Rule (2005): NOx and SO2 2005

Change in ozone standard, 2008

U.S. National Ambient Air Quality standards (NAAQS)

Pollutant	Primary Standards	Averaging Times
Carbon Monoxide	9 ppm (10 mg/m³)	8-hour[1]
	35 ppm (40 mg/m³)	1-hour[1]
Lead	1.5 µg/m³	Quarterly Average
Nitrogen Dioxide	0.053 ppm (100 µg/m³)	Annual (Arithmetic Mean)
Particulate Matter (PM_{10})	Revoked[2]	Annual[2] (Arith. Mean)
	150 µg/m³	24-hour[3]
Particulate Matter ($PM_{2.5}$)	15.0 µg/m³	Annual[4] (Arith. Mean)
	35 µg/m³	24-hour[5]
Ozone	0.08 ppm	8-hour[6]
	0.12 ppm	1-hour[7] (Applies only in limited areas)
Sulfur Oxides	0.03 ppm	Annual (Arith. Mean)
	0.14 ppm	24-hour[1]
	——-	3-hour[1]

(1) Not to be exceeded more than once per year.
(2) Due to a lack of evidence linking health problems to long-term exposure to coarse particle pollution, the agency revoked the annual PM_{10} standard in 2006 (effective December 17, 2006).
(3) Not to be exceeded more than once per year on average over 3 years.
(4) To attain this standard, the 3-year average of the weighted annual mean $PM_{2.5}$ concentrations from single or multiple community-oriented monitors must not exceed 15.0 µg/m³.
(5) To attain this standard, the 3-year average of the 98th percentile of 24-hour concentrations at each population-oriented monitor within an area must not exceed 35 µg/m³ (effective December 17, 2006).
(6) To attain this standard, the 3-year average of the fourth-highest daily maximum 8-hour average ozone concentrations measured at each monitor within an area over each year must not exceed 0.08 ppm.
(7) (a) The standard is attained when the expected number of days per calendar year with maximum hourly average concentrations above 0.12 ppm is ≤ 1, as determined by appendix H.
(b) As of June 15, 2005 EPA revoked the 1-hour ozone standard in all areas except the fourteen 8-hour ozone nonattainment Early Action Compact (EAC) Areas.

EPA: http://www.epa.gov/air/criteria.html

U.S. National Ambient Air Quality standards (NAAQS)

Pollutant	Level	Averaging Time
Carbon Monoxide	9 ppm (10 mg/m^3)	8-hour[1]
	35 ppm (40 mg/m^3)	1-hour[1]
Lead	1.5 µg/m^3	Quarterly Average
Nitrogen Dioxide	0.053 ppm (100 µg/m^3)	Annual (Arithmetic Mean)
Particulate Matter (PM_{10})	150 µg/m^3	24-hour[2]
Particulate Matter ($PM_{2.5}$)	15.0 µg/m^3	Annual[3] (Arithmetic Mean)
	35 µg/m^3	24-hour[4]
Ozone	0.075 ppm (2008 std)	8-hour[5]
	0.08 ppm (1997 std)	8-hour[6]
	0.12 ppm	1-hour[7] (Applies only in limited areas)
Sulfur Dioxide	0.03 ppm	Annual (Arithmetic Mean)
	0.14 ppm	24-hour[1]

[5] To attain this standard, the 3-year average of the fourth-highest daily maximum 8-hour average ozone concentrations measured at each monitor within an area over each year must not exceed 0.075 ppm. (effective May 27, 2008)

EPA: http://www.epa.gov/air/criteria.html

U.S. National Ambient Air Quality standards (NAAQS)

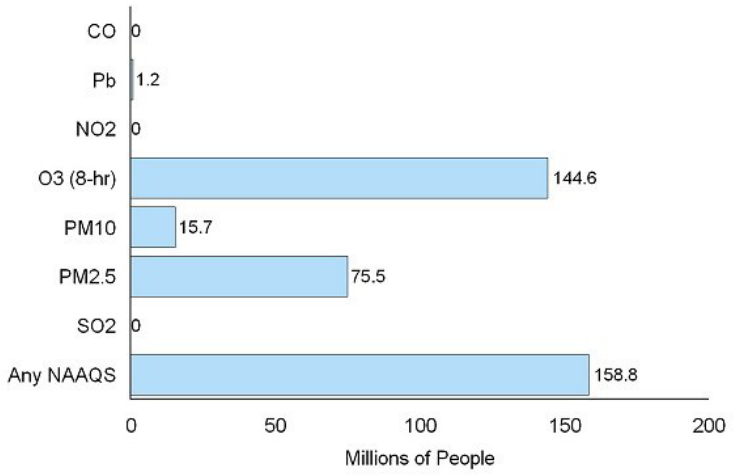
[1] Not to be exceeded more than once per year.
[2] Not to be exceeded more than once per year on average over 3 years.
[3] To attain this standard, the 3-year average of the weighted annual mean PM2.5 concentrations from single or multiple community-oriented monitors must not exceed 15.0 µg/m3.
[4] To attain this standard, the 3-year average of the 98th percentile of 24-hour concentrations at each population-oriented monitor within an area must not exceed 35 µg/m3 (effective December 17, 2006).
[5] To attain this standard, the 3-year average of the fourth-highest daily maximum 8-hour average ozone concentrations measured at each monitor within an area over each year must not exceed 0.075 ppm. (effective May 27, 2008)
[6] (a) To attain this standard, the 3-year average of the fourth-highest daily maximum 8-hour average ozone concentrations measured at each monitor within an area over each year must not exceed 0.08 ppm.

(b) The 1997 standard—and the implementation rules for that standard—will remain in place for implementation purposes as EPA undertakes rulemaking to address the transition from the 1997 ozone standard to the 2008 ozone standard.
[7] (a) The standard is attained when the expected number of days per calendar year with maximum hourly average concentrations above 0.12 ppm is ≤ 1.

(b) As of June 15, 2005 EPA revoked the 1-hour ozone standard in all areas except the 8-hour ozone nonattainment Early Action Compact (EAC) Areas.

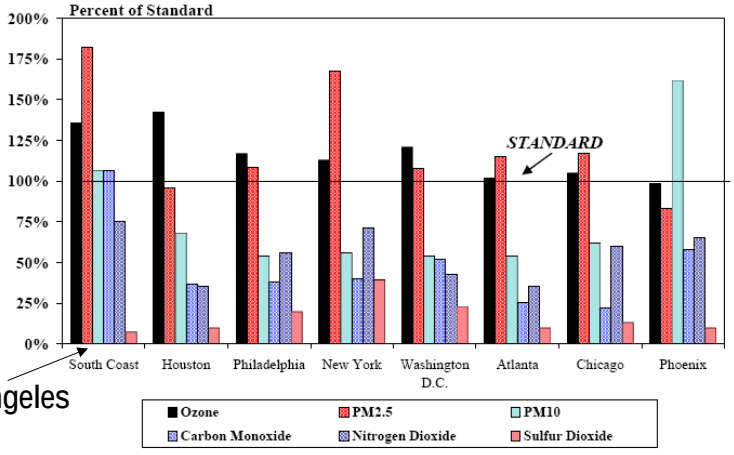
EPA: http://www.epa.gov/air/criteria.html

Number of people living in US counties violating the EPA air quality standards in 2007



http://www.epa.gov/air/airtrends/sixpoll.html

Maximum Pollutant concentration in Major U.S. Metropolitan Areas (2002)

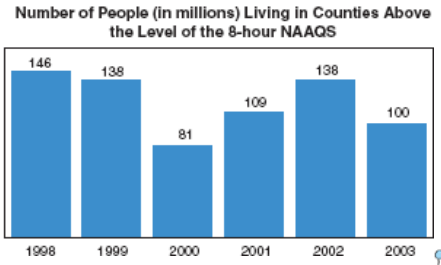


Los Angeles

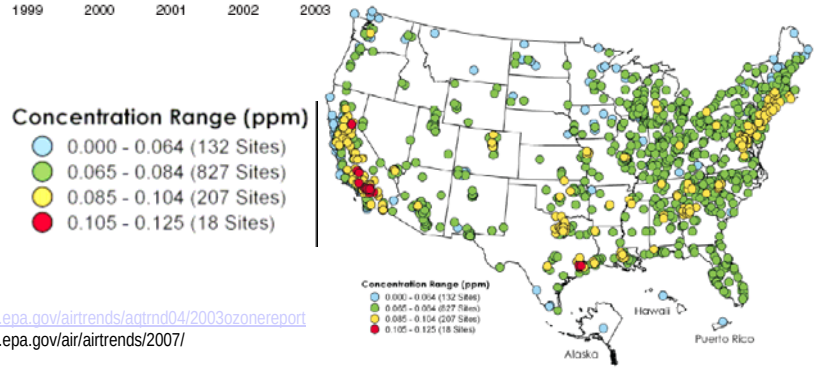
Figure 2
Maximum Pollutant Concentrations as Percent of Federal Standards
South Coast Air Basin Compared to U.S. Metropolitan Areas

South Coast AQMD
http://www.aqmd.gov/smog/AQSCR2002/aq02web.pdf

Ozone (8-hour) non-attainment areas in US



4th highest O3 concentrations (2006)



EPA:
http://www.epa.gov/airtrends/aqtrnd04/2003ozonereport
http://www.epa.gov/air/airtrends/2007/

Time series of ozone concentrations measured in Boston

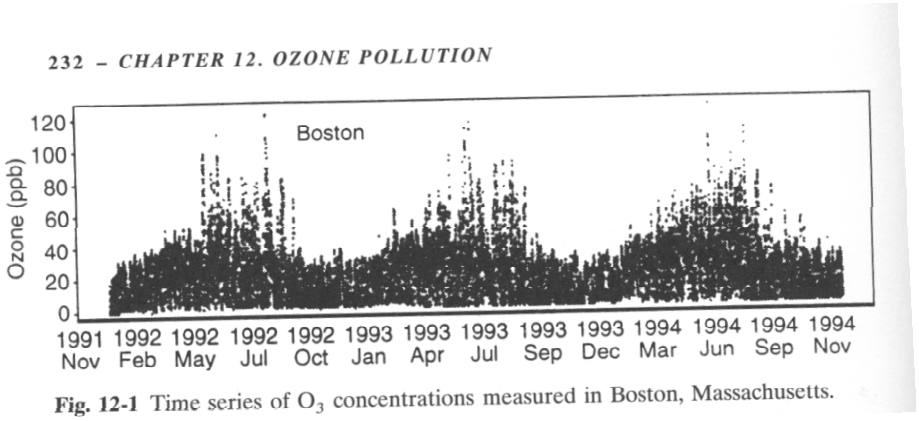
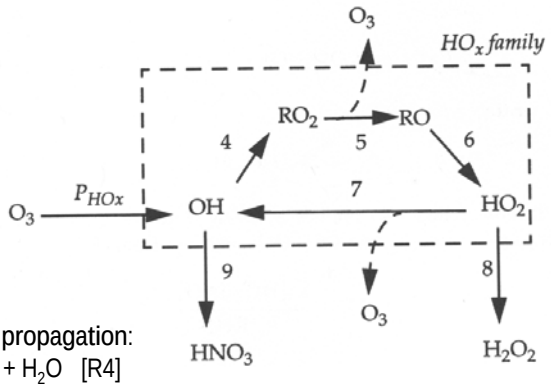


Fig. 12-1 Time series of O_3 concentrations measured in Boston, Massachusetts.

Ozone pollution season: June-August

Ozone production



Chain initiation and propagation:

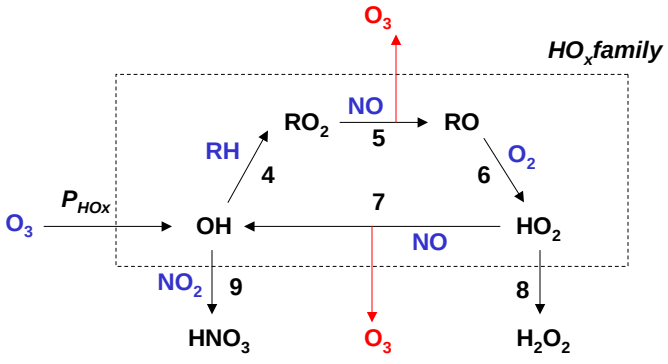
$RH + OH + O_2 \rightarrow RO_2 + H_2O$ [R4]
$RO_2 + NO \rightarrow RO + NO_2$ [R5]
$RO + O_2 \rightarrow R'CHO + HO_2$ [R6]
$HO_2 + NO \rightarrow OH + NO_2$ [R7]
$2(NO_2 + h\nu\ (+O_2) \rightarrow NO + O_3)$

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

Chain termination

$HO_2 + HO_2 \rightarrow H_2O_2$ [R8]
$OH + NO_2 + M \rightarrow HNO_3 + M$ [R9]

DEPENDENCE OF OZONE PRODUCTION ON NO_x AND HYDROCARBONS



$$P(O_3) = \frac{2k_4 P_{HOx}[RH]}{k_9[NO_2][M]}$$

"NO_x- saturated" or "hydrocarbon-limited" regime

$$P(O_3) = 2k_7 \left(\frac{P_{HOx}}{2k_8}\right)^{1/2}[NO]$$

"NO_x-limited" regime

Dependence of ozone production on hydrocarbon and NOx emissions

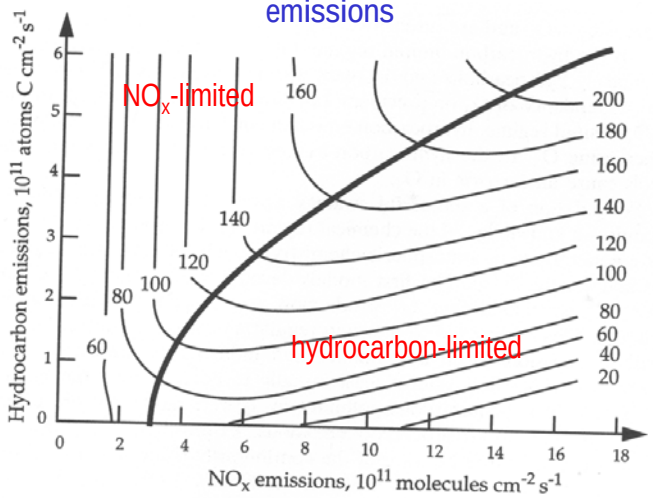


Fig. 12-4 Ozone concentrations (ppbv) simulated by a regional photochemical model as a function of NO_x and hydrocarbon emissions. The thick line separates the NO_x-limited (top left) and hydrocarbon-limited (bottom right) regimes. Adapted from Sillman, S., J. A. Logan, and S. C. Wofsy. *J. Geophys. Res.* 95:1837–1852, 1990.

Ozone control strategies

- Initial models in the 1970s showed that O_3 production was generally hydrocarbon limited
- Emphasis has been on reducing hydrocarbon emissions

➔ 12% decrease in hydrocarbon emissions between 1980 and 1995 but constant NO_x emissions (20% population growth and 60% increase in car usage)

➔ Result: Mixed success. Improvements in air quality for worst offenders (Los Angeles basin + New York metropolitan area) but no improvement elsewhere

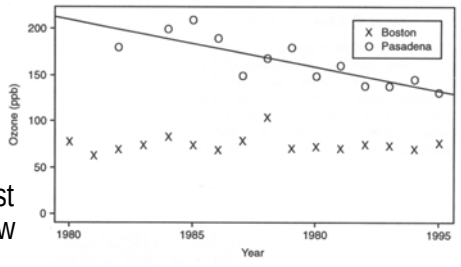


Fig. 12-5 Long-term trends in the ninetieth percentile summer afternoon concentrations of O_3 in Pasadena (Los Angeles Basin) and Boston for the period 1980–1995. There is a significant decreasing trend in Pasadena (the regression line is shown) but no significant trend in Boston. The high 1988 concentrations in Boston were due to anomalously stagnant weather over the eastern United States that summer. From Fiore, A. M., D. J. Jacob, J. A. Logan, and J. H. Yin. *J. Geophys. Res.* 103:1471–1480, 1998.

NOx and VOC emissions in the U.S. since 1970

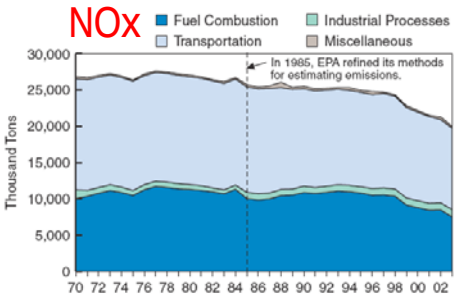


Figure 12. National Trends in NO_x Emissions, 1970–2003.

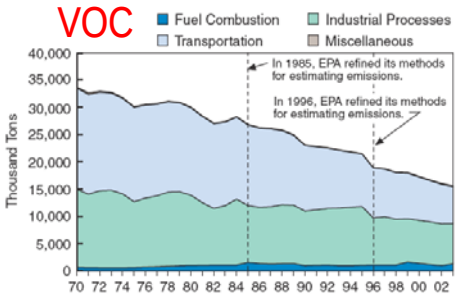


Figure 13. National Trends in VOC Emissions, 1970–2003.

Growth areas and emissions

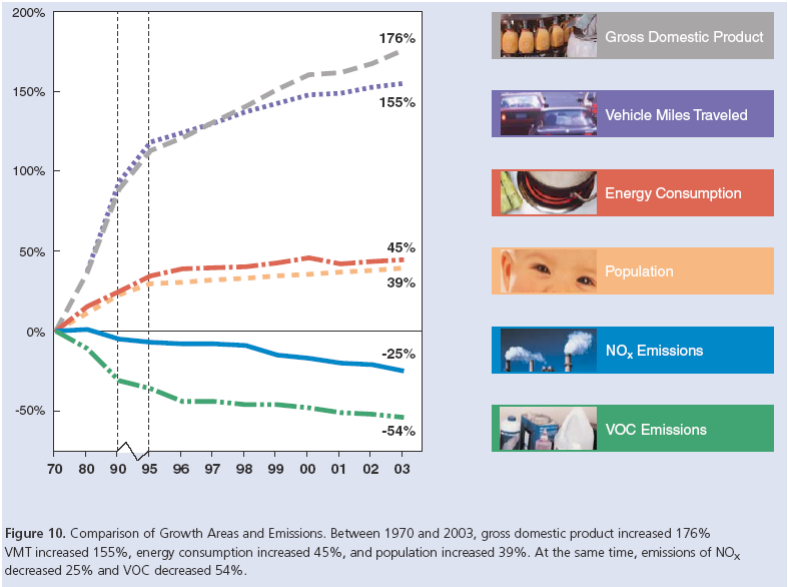
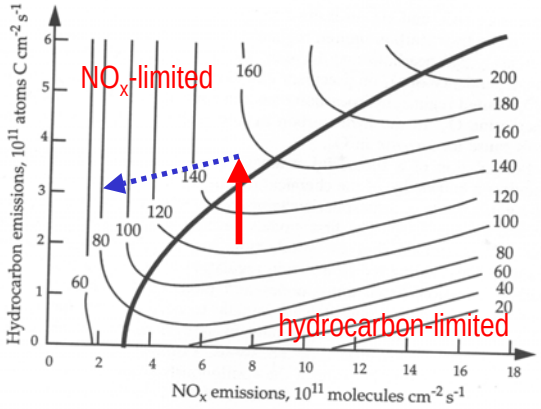


Figure 10. Comparison of Growth Areas and Emissions. Between 1970 and 2003, gross domestic product increased 176% VMT increased 155%, energy consumption increased 45%, and population increased 39%. At the same time, emissions of NO_x decreased 25% and VOC decreased 54%.

EPA's ozone report, 2003

Ozone control strategies (cont.)

- Now models show that ozone production over most of the U.S. is NOx-limited.
- Initial results were wrong because of underestimate of hydrocarbon emissions from cars + did not take into account biogenic hydrocarbon emissions from trees and crops.



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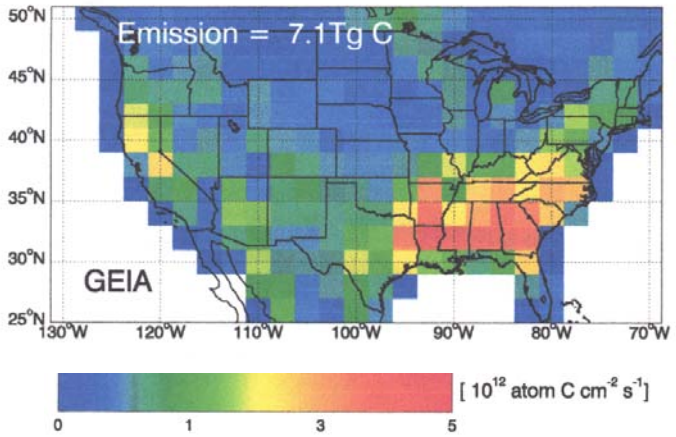
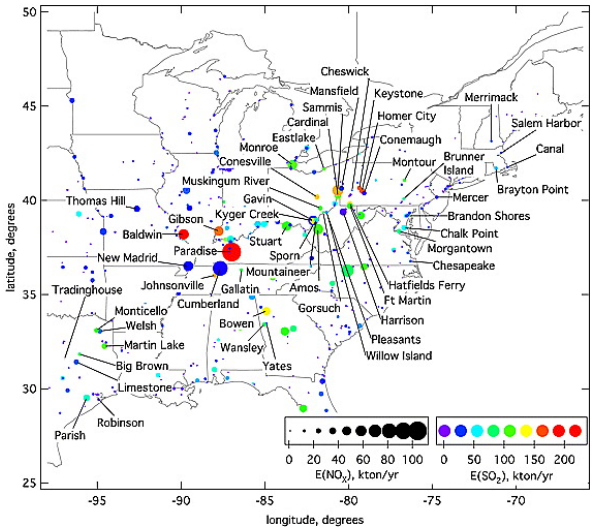
Isoprene emissions over the U.S.



Palmer et al., 2001
Isoprene emissions
For July 1996

"Trees cause more pollution than automobiles do." – Ronald Reagan, 1981

Point emission sources in the eastern United States (1999)



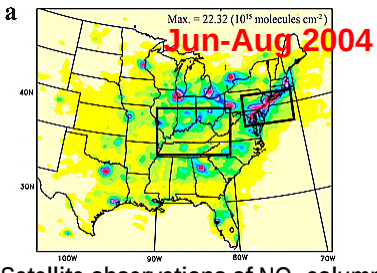
Power plants ~25% all US NOx emissions

1998 NOx state implementation plan: Reduction in NOx emission from power plants in Eastern US
50% in 2004 compared to 2000 levels

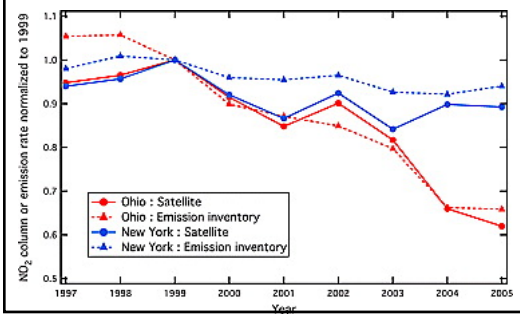
Frost et al. (2006), JGR.

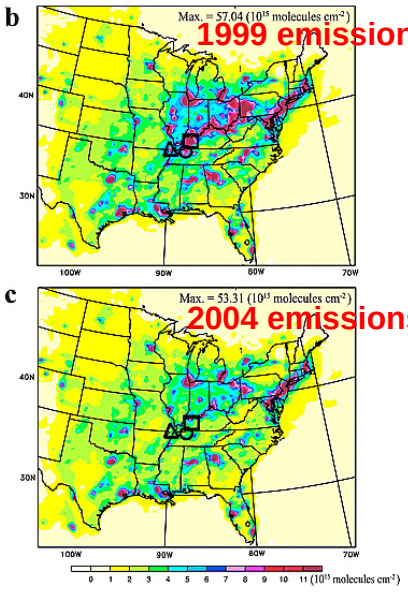
Satellite-observed U.S. power plant NO_x emission reductions

Kim et al., GRL, 2006.



Satellite observations of NO_2 columns





Model calculated NO_2 columns