Lecture 5
Ground-level Ozone
(also called "photochemical smog")

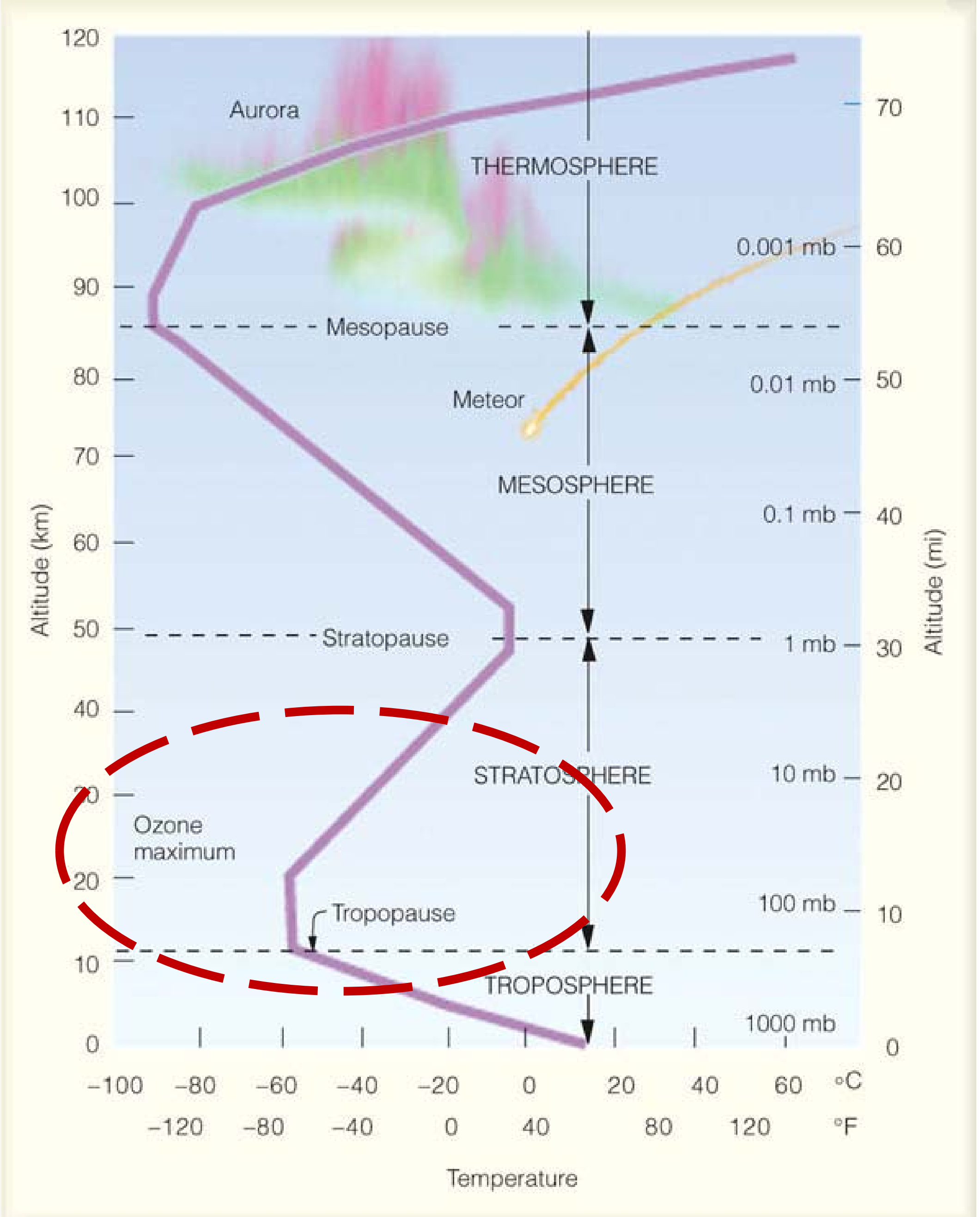
METR 113/ENVS 113
Spring Semester 2011
April 12, 2011

Reading …

- Jacobson, Chapter 4 (Ozone "smog" - Troposphere)
- Review
  - Jacobson Chapter 7 (Radiation)
  - Jacobson Chapter 11 (Ozone Layer – Stratosphere)
- Turco, Chapter 6

Remember from Lecture 2 …

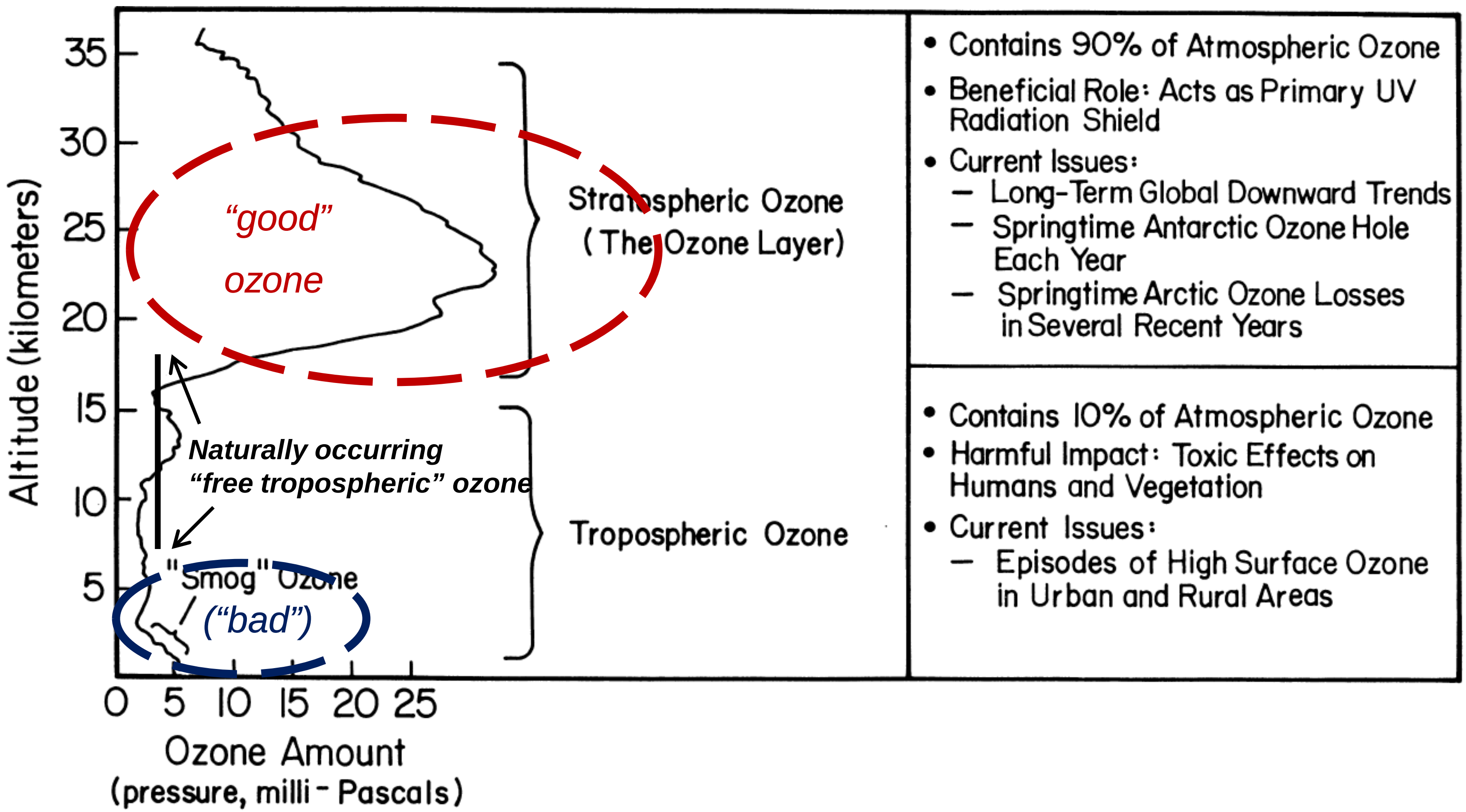
Vertical Variation of Temperature (on average around the earth)



<u>Troposphere</u> – Lowest ~ 10km, weather systems

<u>Stratosphere</u> – 10 – 50 km, ozone layer

From Lecture 2: Ozone (O_3) Concentration vs. Height



- **Tropospheric ozone concentrations due to industrial air pollution ("smog")**
- **Stratospheric ozone concentrations comprise the "ozone layer".**
- **We are concerned with "smog" ozone in this lecture**

Chemical Reactions

Given chemical species A, B, C & D…

$$A + B \rightarrow C + D$$

A reacts with B to produce C and D

– A & B are “reactants”

– C & D are “products”

Photochemical Reactions

Given chemical species A, B & C …

$$A + h\nu \rightarrow B + C,$$

where ‘hν’ is the energy absorbed by A from sunlight.

‘A’ absorbs sunlight and is chemically broken down to produce ‘B’ and ‘C’.

Ozone Formation in Stratosphere

(review from Lecture 2 whiteboard illustration …)

Formation Mechanism …

O_2 + hv → O + O (Protection from uv-rad at surface)

O_2 + O → O_3

Absorption of uv by ozone …

O_3 + hv → O_2 + O (Protection from uv-rad at surface)

See Jacobson, Chapter 11.1-11.3

Ozone in Free Troposphere (Natural)

- "Background" tropospheric concentration ~ 10-40 ppb
- Maintained in the troposphere by …
  - Mixing of stratospheric ozone into troposphere
  - Chemical/photochemical reactions involving NO and NO_2 (NO_x)

Chemical Formation …

Source

$NO_2 + h\nu \rightarrow NO + O$ ($\lambda < 420$ nm)

$O_2 + O \rightarrow O_3$

Sink

$NO + O_3 \rightarrow NO_2 + O_2$

Forming ozone at about the rate that it is being destroyed. Source balance sinks. Therefore, more or less a constant amount of ozone in the free troposphere at concentration of 10-40 ppb.

Nitrogen Dioxide (NO_2) “cloud”

NO_2 →

- NO_2 absorbs blue & green visible wavelengths
- Lets yellow, orange & red wavelengths pass through
- Visible to eye as “brown”

NO_x Sources (Tg Nitrogen per Year)

Technological	23 - 27
Aircraft	0.5
Biomass burning	7.0 - 8.0
Soils	5.0 - 12.0
Lightning	3.0 - 20.0

NATURAL SOURCES …

- Biomass burning, wildfires
  - includes savannah burning, tropical deforestation, temperate wildfires and agricultural waste burning
- Soil emission
  - enhanced by application of fertilizers
- Lightning
- See also Lecture 3 (global nitrogen cycle)

Tropospheric Ozone

(ground-level ozone “smog”)

- Elevated ozone levels in many polluted urban environments
- Especially prevalent in summer, warm & sunny weather, daytime
- Formed from chemical rxns involving NO_x & “hydrocarbons” (HC)
- NO_x & HCs are ozone “precursors”
- Hydrocarbons are organic gases
  - Organic compound - Involve C-H bonds
  - Examples: Methane (CH_4), Benzene (C_6H_6), many others …
  - Also called: Volatile Organic Compounds (VOCs)
  - Also called: Reactive Organic Gases (ROGs)

Hydrocarbons

Specific Groups …

a) Alkanes (ethane, propane, butane, etc …)
b) Alkenes (butene, ethene)
c) Aromatics (e.g., toluene, xylene, benzene)
d) Terpenes (biogenic emissions)
e) Alcohol (e.g., ethanol, methanol)
f) Aldehydes (formaldehyde, others …)

Terminology

a) Reactive hydrocarbons (RH)
b) Non-methane Hydrocarbons (NMHC)
c) Reactive Organic Gases (ROG)
d) Volatile Organic Compounds (VOC)

Chemical reactions over time break down organic gases to CO_2

For example, alkanes …

- CH_4: Methane
- C_2H_6: Ethane
- C_3H_8: Propane
- C_4H_{10}: Butane
- C_5H_{12}: Pentane
- C_8H_{18}: Octane

Hydrocarbon Sources

(Example: San Joaquin Valley)

List of Top 25 ROG Sources in the San Joaquin Valley Air Basin

Rankings		Summer Emissions:	1999		2010	
1999	*2010*	SOURCE CATEGORY	*ROG (tpd)*	*% of Total*	*ROG (tpd)*	*% of Total*
4	1	LIVESTOCK WASTE (DAIRY CATTLE)	31.6	7.0%	44.1	12.0%
3	2	OIL AND GAS PRODUCTION (EVAPORATIVE LOSSES)	32.4	7.2%	31.4	8.6%
5	3	PRESCRIBED BURNING	27.9	6.2%	26.9	7.3%
7	4	CONSUMER PRODUCTS	25.9	5.8%	26.7	7.3%
2	5	LIGHT AND MEDIUM DUTY TRUCKS	49.2	11.0%	25.7	7.0%
6	6	PESTICIDES	26.9	6.0%	23.4	6.4%
1	7	LIGHT DUTY PASSENGER CARS	51.5	11.5%	19.2	5.2%
12	8	COATINGS (PAINTS AND THINNERS - NON ARCHITECTURAL)	13.6	3.0%	17.5	4.8%
16	9	AIRCRAFT	11.0	2.4%	13.2	3.6%
10	10	ARCHITECTURAL COATINGS (PAINTS AND THINNERS)	14.0	3.1%	13.1	3.6%
13	11	LIVESTOCK WASTE (POULTRY)	12.4	2.8%	12.4	3.4%
17	12	FOOD AND AGRICULTURE (CROP PROCESSING AND WINERIES)	10.6	2.4%	11.8	3.2%
8	13	RECREATIONAL BOATS	19.3	4.3%	10.4	2.9%
11	14	OFF-ROAD EQUIPMENT (LAWN/GARDEN, CONSTRUCTION, ETC)	13.8	3.1%	8.3	2.3%
20	15	PETROLEUM MARKETING (GASOLINE EVAPORATIVE LOSSES)	6.5	1.4%	8.0	2.2%
15	16	FARM EQUIPMENT (TRACTORS)	11.0	2.5%	7.3	2.0%
19	17	LIVESTOCK WASTE (RANGE CATTLE)	6.8	1.5%	6.8	1.9%
21	18	AG BURNING	6.0	1.3%	5.8	1.6%
9	19	HEAVY DUTY GAS TRUCKS	15.4	3.4%	5.5	1.5%
23	20	LIVESTOCK WASTE (FEED LOT CATTLE)	4.8	1.1%	4.8	1.3%
22	21	HEAVY DUTY DIESEL TRUCKS	4.8	1.1%	4.2	1.2%
27	22	OTHER (CLEANING AND SURFACE COATINGS)	2.7	0.6%	4.0	1.1%
26	23	LANDFILLS (LANDFILL GAS EMISSIONS)	2.7	0.6%	3.4	0.9%
25	24	OIL AND GAS PRODUCTION (COMBUSTION)	2.7	0.6%	3.2	0.9%
24	25	ASPHALT PAVING / ROOFING	2.8	0.6%	3.0	0.8%
		TOTAL OF TOP 25	**406.3**	**90.5%**	**340.2**	**92.9%**
This inventory taken from CEIDARS (May 2003), OFFROAD Model (September 2002) and EMFAC 2002 v. 2.2 (September 2002)						
Shared on 'Cluster_usersa_server\Usersa\Ptsd\Branch\Eib'\1-EIA section\LHunsaker\Top 25\Top 25 SJV (May 2003).xls						

Urban Ozone Chemistry …

$NO + ROG^* \rightarrow NO_2 + ROG^{**}$
$NO + ROG^{**} \rightarrow NO_2 + ROG^{***}$
$NO + ROG^{***} \rightarrow NO_2 + ROG^{****}$

$NO + O_3 \rightarrow NO_2 + O_2$
$NO_2 + h\nu \rightarrow NO + O$ ($\lambda < 420$ nm)
$O_2 + O \rightarrow O_3$

- Reactions with organics provide additional pathways to produce NO_2 that do not consume O_3

- Breakdown (oxydation) of organic gases:
  $ROG^* \rightarrow ROG^{**} \rightarrow ROG^{***} \rightarrow \ldots \rightarrow CO$ & CO_2

- Notes …
  - Sunlight is required to break down NO_2
  - Chemical reaction rates increase with temperature.
  - Therefore, higher O_3 concentrations during hot days (typically …)

Reactivity of ROGs …

Table 11.6 Ranking of the most abundant species in terms of reactivity during the summer Southern California Air Quality Study in 1987

1. *m*- and *p*-Xylene	8. *o*-Xylene	15. *m*-Ethyltoluene	22. *p*-Ethyltoluene
2. Ethene	9. Butane	16. Pentanal	23. C_4 Olefin
3. Acetaldehyde	10. Methylcyclopentane	17. Propane	24. 3-Methylpentane
4. Toluene	11. 2-Methylpentane	18. Propanal	25. *o*-Ethyltoluene
5. Formaldehyde	12. Pentane	19. *i*-Butane	
6. *i*-Pentane	13. 1,2,4-Trimethylbenzene	20. C_6 Carbonyl	
7. Propene	14. Benzene	21. Ethylbenzene	

Source: Lurmann *et al*. (1992). The ranking was determined by multiplying the weight fraction of each organic present in the atmosphere by a species-specific reactivity scaling factor developed by Carter (1991).

By "reactivity" or ROG, we mean essentially how long is following chain …
ROG* → ROG** → ROG***→ …→ CO & $CO_{2.}$

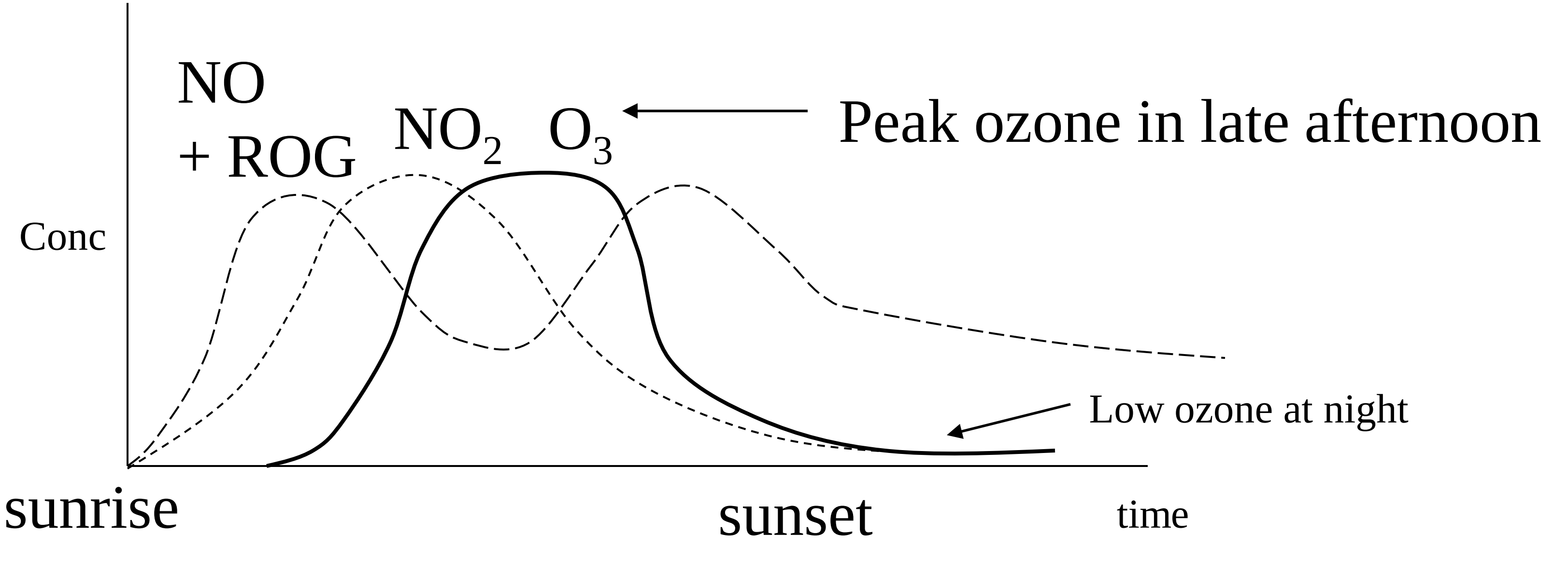
The longer the chain, the more NO to NO_2 conversions there are, and the more ozone is formed provided sunlight is available to breakdown NO_2 to O_3.

From Jacobson, M. Z., "Fundamentals of Atmospheric Modeling"

Diurnal Cycle of Ozone Concentration …

$NO + ROG^* \rightarrow NO_2 + ROG^{**}$
$NO + O_3 \rightarrow NO_2 + O_2$
$NO_2 + h\nu \rightarrow NO + O$ $(\lambda < 420\ nm)$
$O_2 + O \rightarrow O_3$

Diurnal variation of emissions of NO & ROG (cars & industry)
+ Diurnal variation of sunlight …



Observations over LA Basin

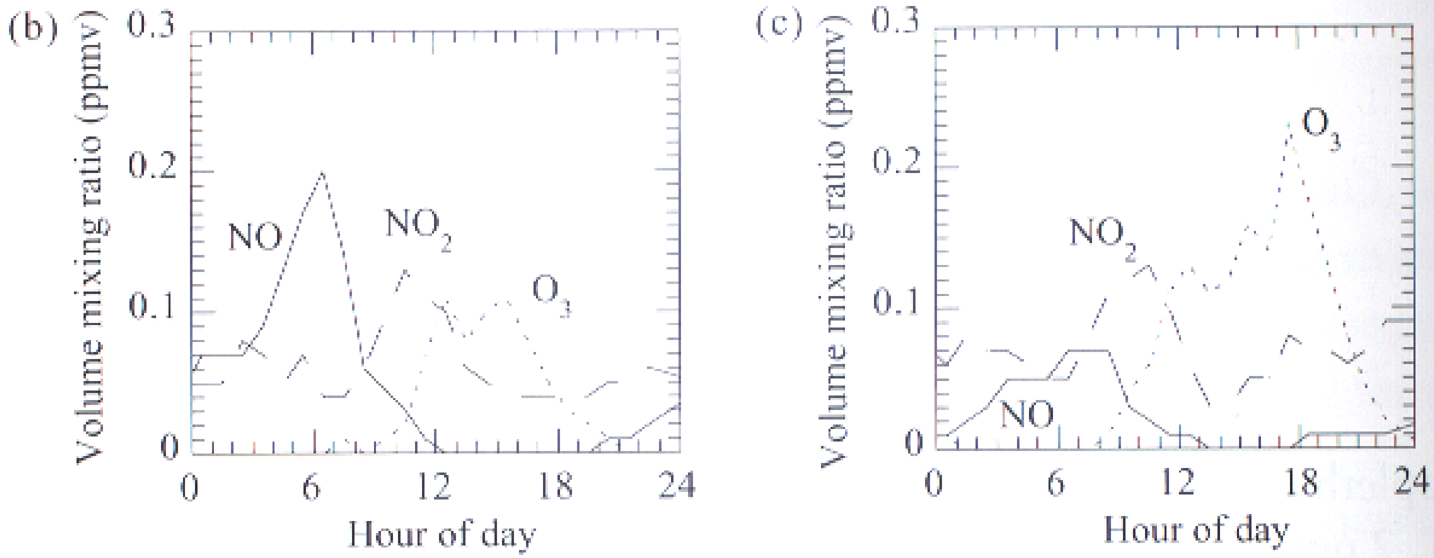
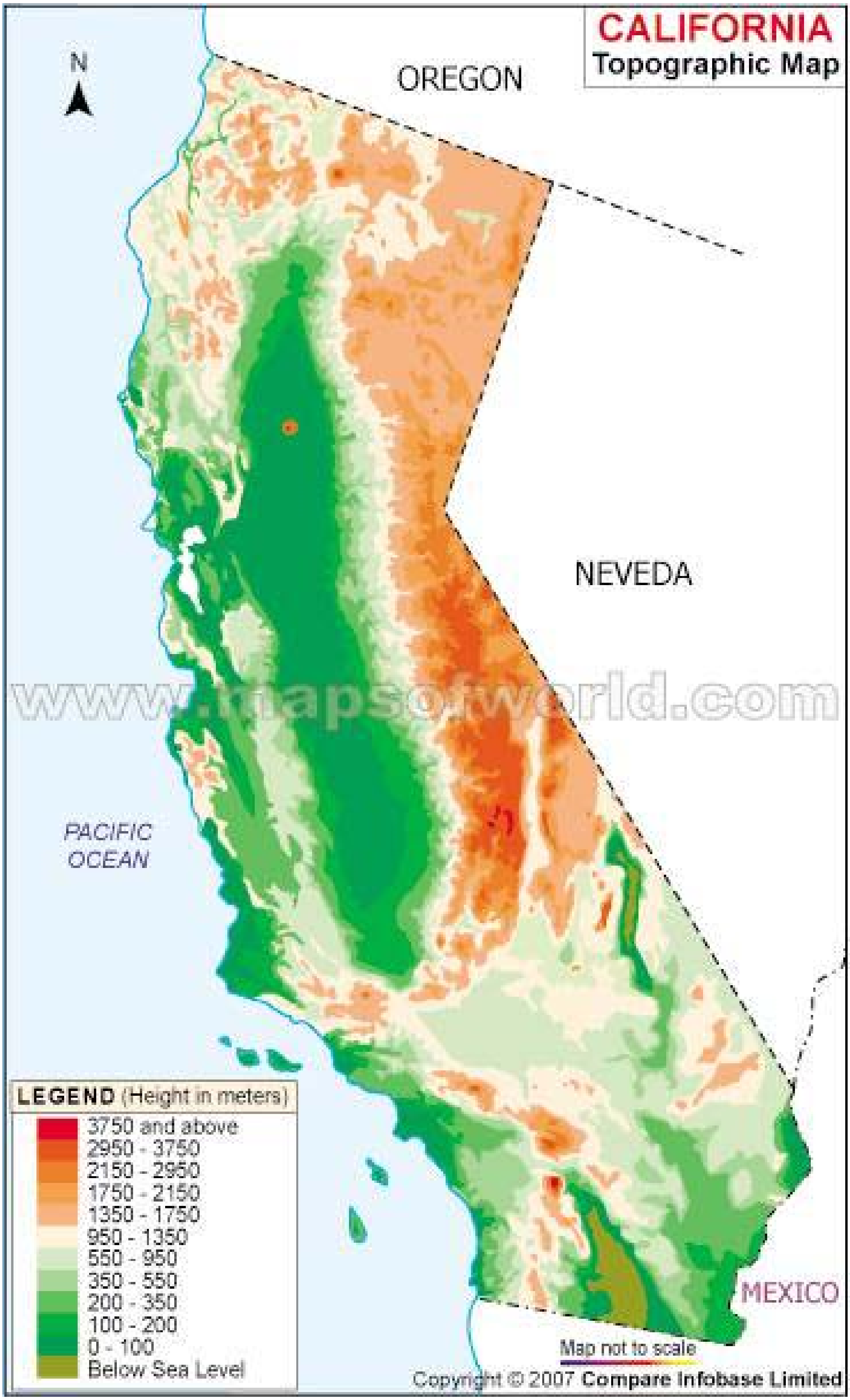


Figure 11.2 (a) Wind speeds at Hawthorne from August 26 to 28, 1987. The other panels show the evolution of the NO, NO_2, and O_3 mixing ratios at (b) central Los Angeles and (c) San Bernardino on August 28. Central Los Angeles is closer to the coast than is San Bernardino. As the sea breeze picks up during the day, primary pollutants, such as NO, are transported from the western side of the Los Angeles basin (e.g., central Los Angeles) toward the eastern side (e.g., San Bernardino). As the pollution travels, organic peroxy radicals convert NO to NO_2, which forms ozone, a secondary pollutant.

From Jacobson, M. Z., "Fundamentals of Atmospheric Modeling"


CALIFORNIA
Topographic Map
N
OREGON
NEVEDA
PACIFIC OCEAN
MEXICO
LEGEND (Height in meters)
3750 and above
2950 - 3750
2150 - 2950
1750 - 2150
1350 - 1750
950 - 1350
550 - 950
350 - 550
200 - 350
100 - 200
0 - 100
Below Sea Level
Map not to scale
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Transport Patterns: Bay Area

FIGURE 3.4-5
Ozone Transport from the BAAQMD

Transport Patterns: California

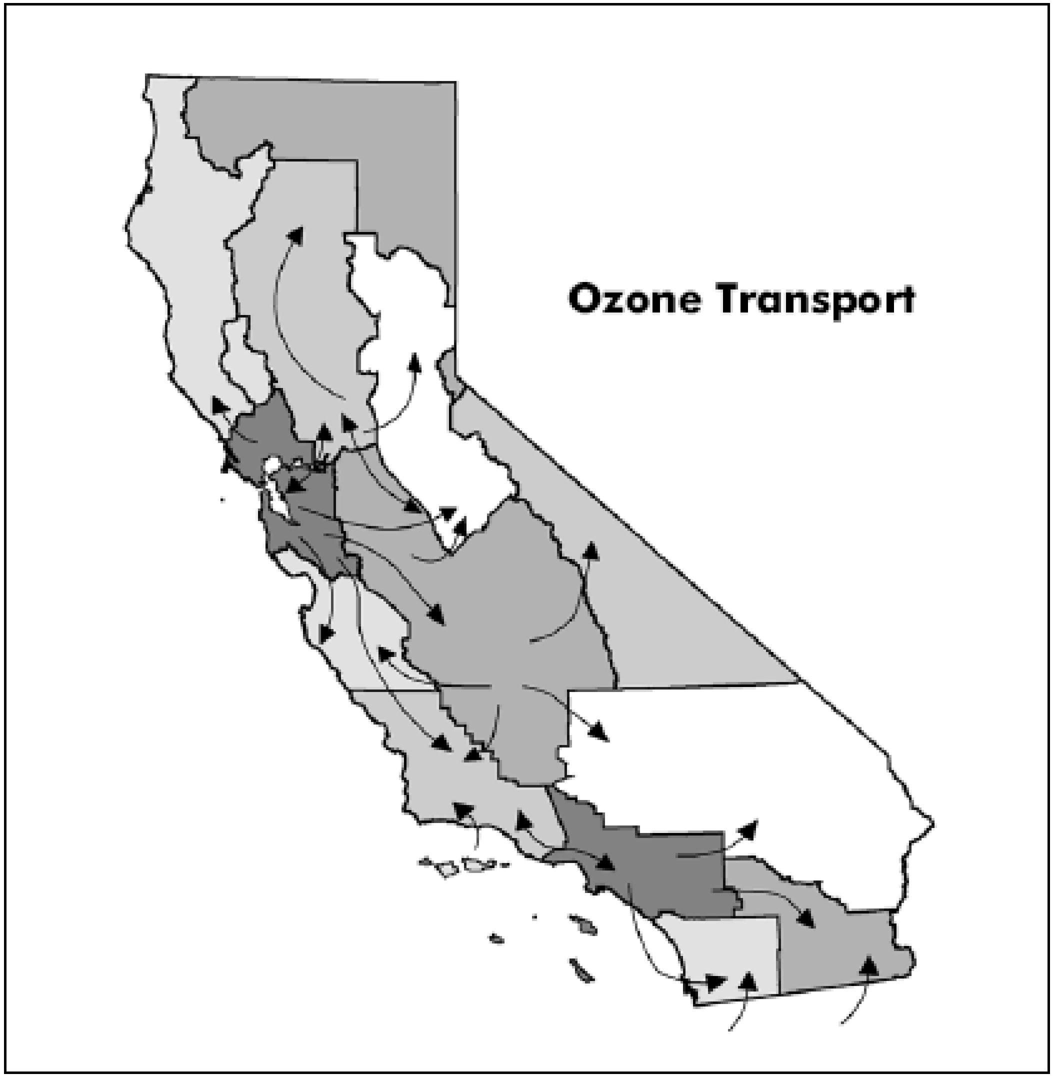


Figure 3-6

Transport Patterns: California

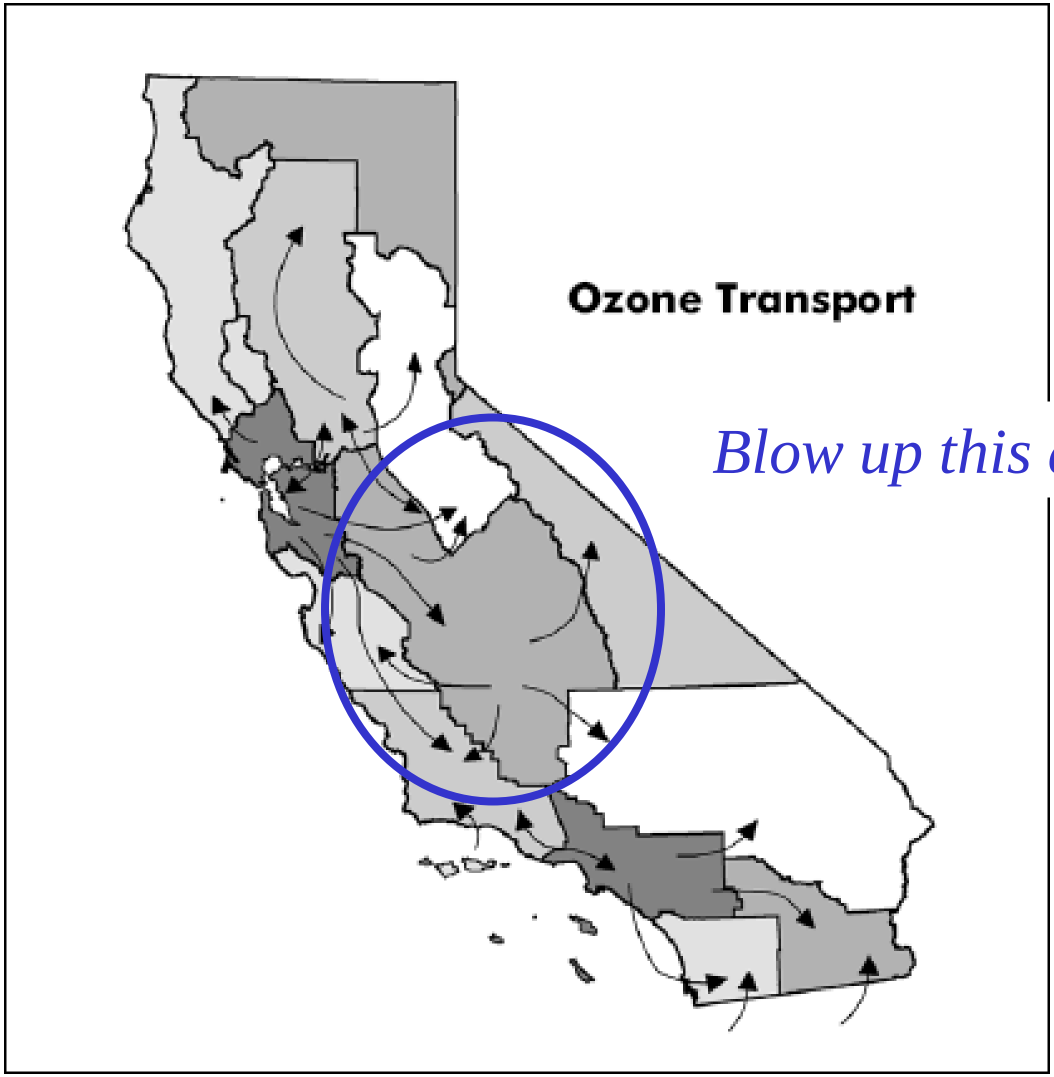
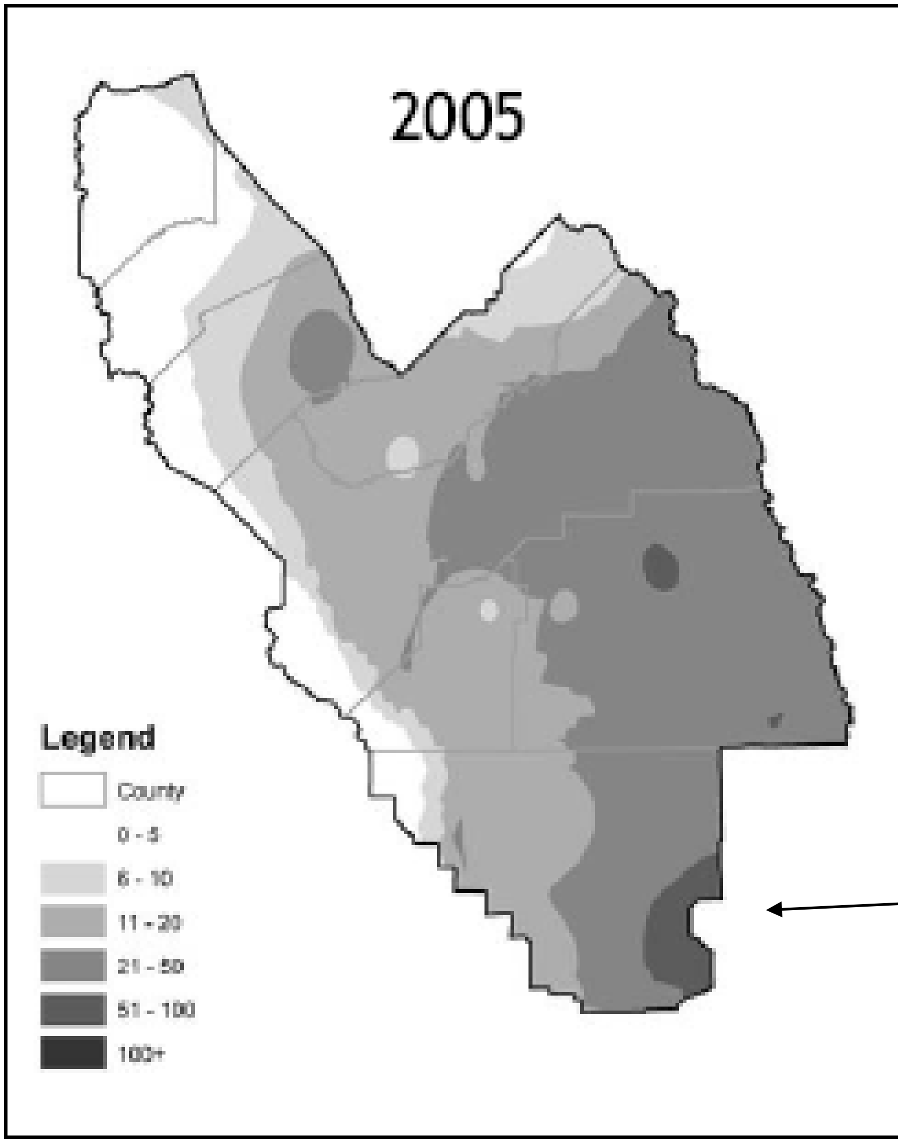


Figure 3-6

Blow up this area (next slide) …

San Joaquin Valley
Number of Days Exceeding NAAQS 8-hour Ozone Standard



Peak in Southern
San Joaquin Valley

Long Range Transport Issues …

- Some of the ozone precursors for a given region (“Region 2”) can be emitted upwind in another region (“Region 1”).
- Precursors blow downwind from Region 1 to Region 2. Form some of the ozone in Region 2.
- Can be a regulatory problem … i.e. who’s to blame for ozone exceedances?
- Problem areas: Central Valley (CA), Eastern seaboard (Connecticut via NYC emissions?), others …
- See http://www.arb.ca.gov/aqd/transport/transport.htm

Nighttime Ozone Removal

No sunlight, no uv-absorption by NO_2 to form O_3

removed through various reactions (not shown)

$$NO + ROG^* \rightarrow NO_2 + ROG^{**}$$

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

$$NO_2 + h\nu \rightarrow NO + O \qquad (\lambda < 420\ \text{nm})$$

$$O_2 + O \rightarrow O_3$$

Notes …

- “Fresh” NO emissions at night chemically react with O_3
- No sunlight to form free oxygen (O) from NO_2 to reform O_3
- Therefore, reduced ozone at night
- In addition, various reactions (not shown) reduce NO_2 concentrations at night

Improvements in California Air Quality …

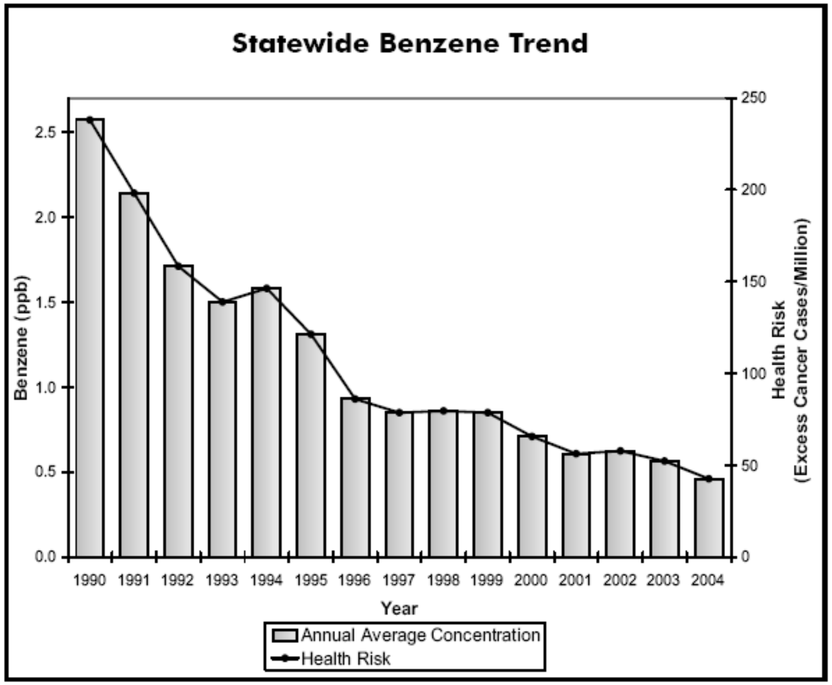


Figure 5-3

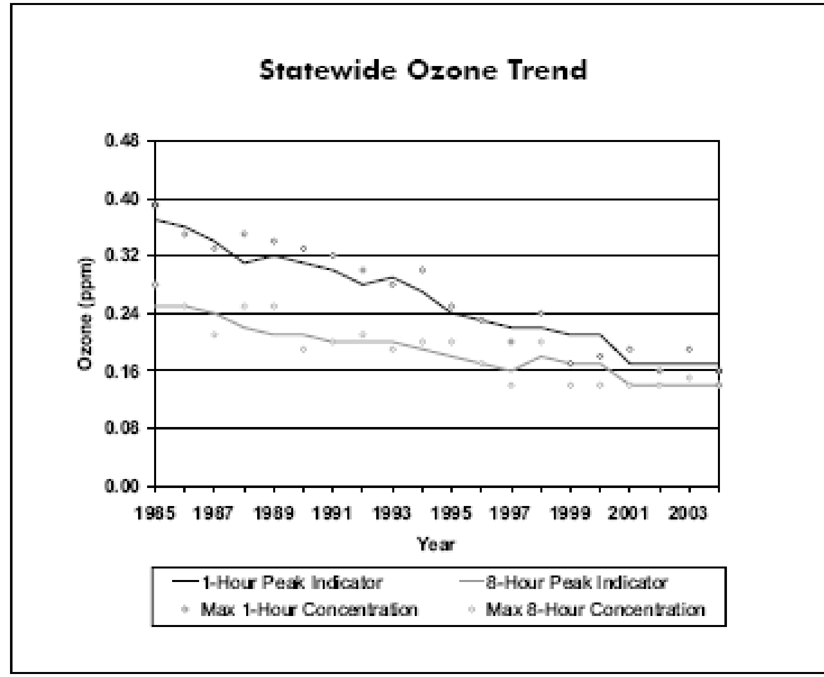


Figure 3-4

BENZENE

(an ROG, and therefore an ozone precursor)

OZONE