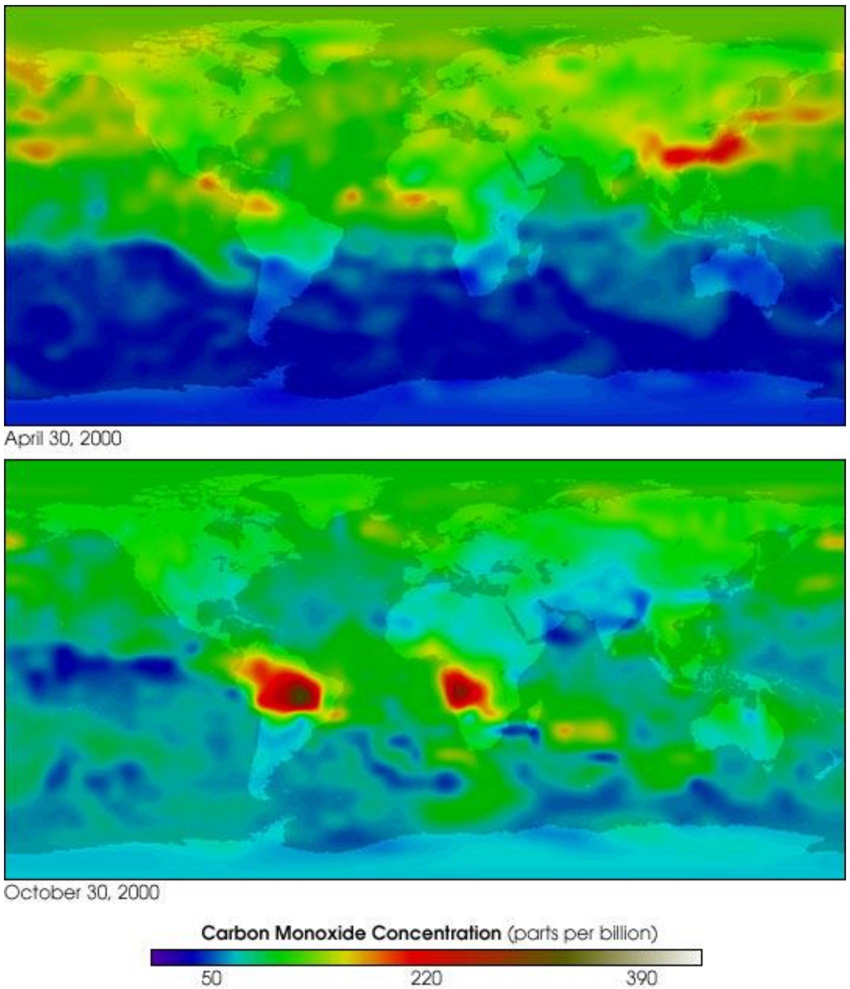


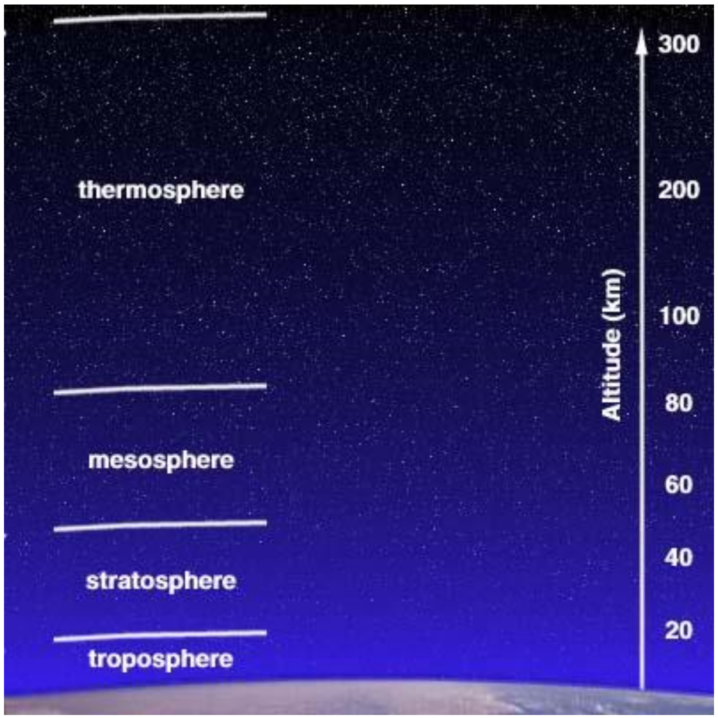
Tropospheric Chemistry and Ground Level Ozone

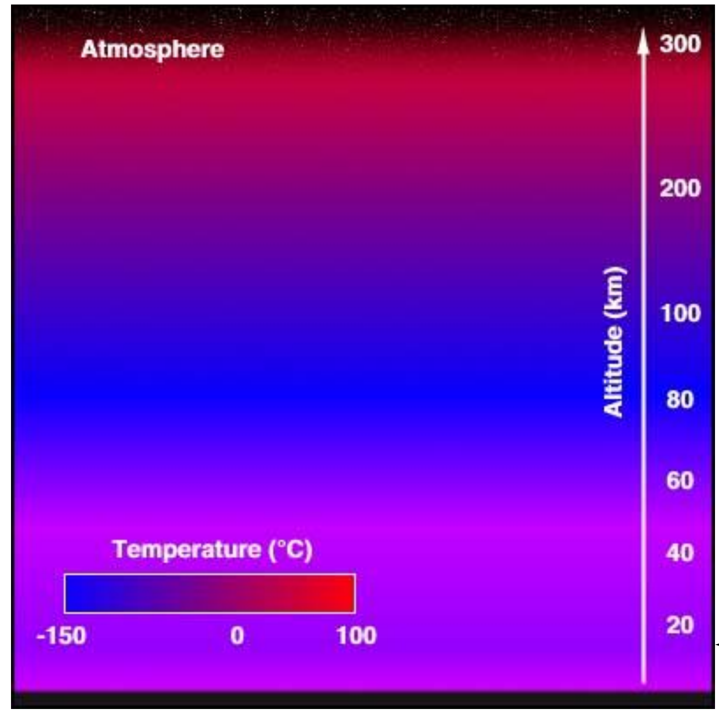
Tropospheric Chemistry:

- The Formation of Ground Level Ozone
- Ozone Modeling and Air Quality
- Role of Trees in Ozone Formation

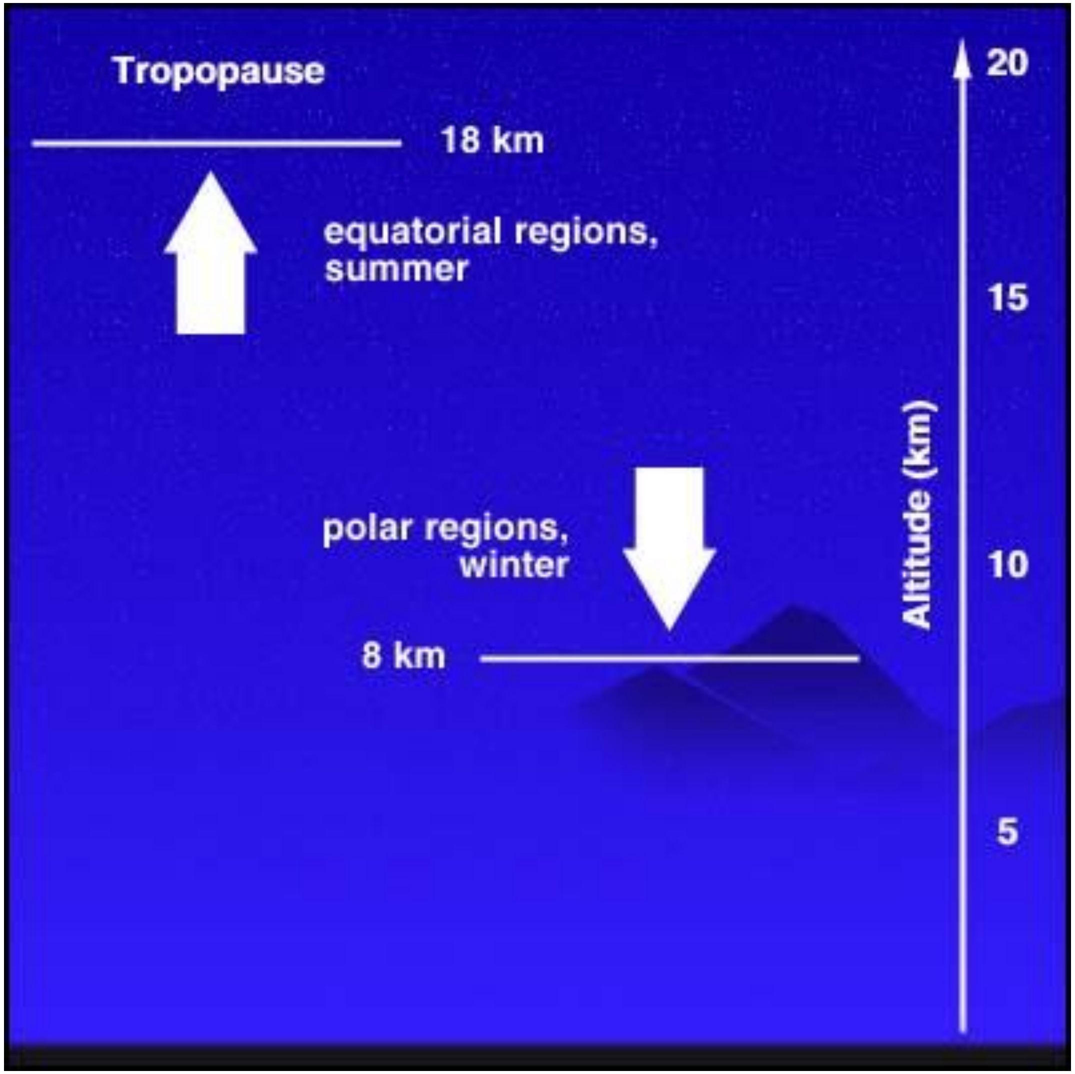
Reading:
Chapters 4&6 Environmental Chemistry, G. W. vanLoon. S. J. Duffy

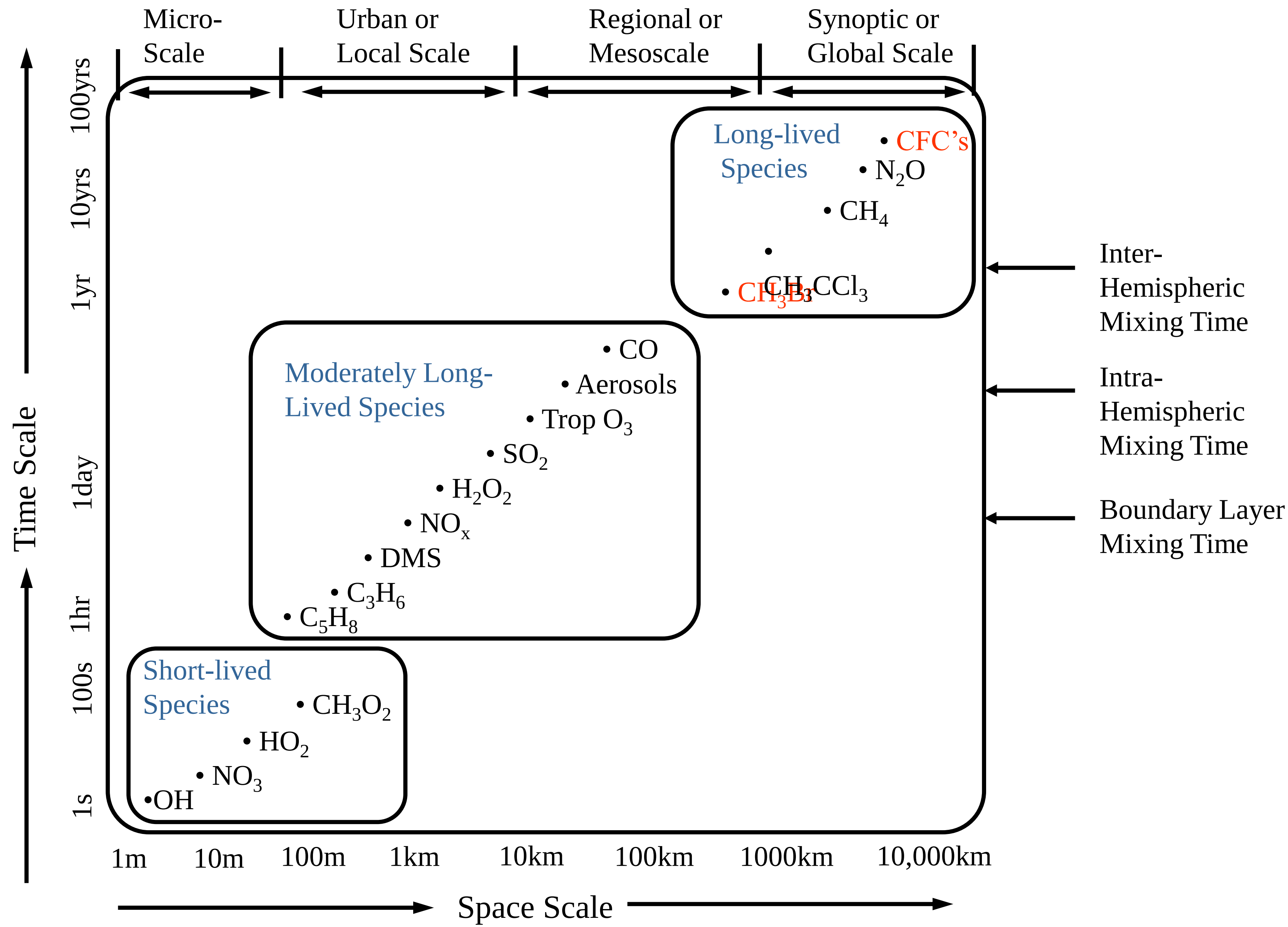
The Troposphere



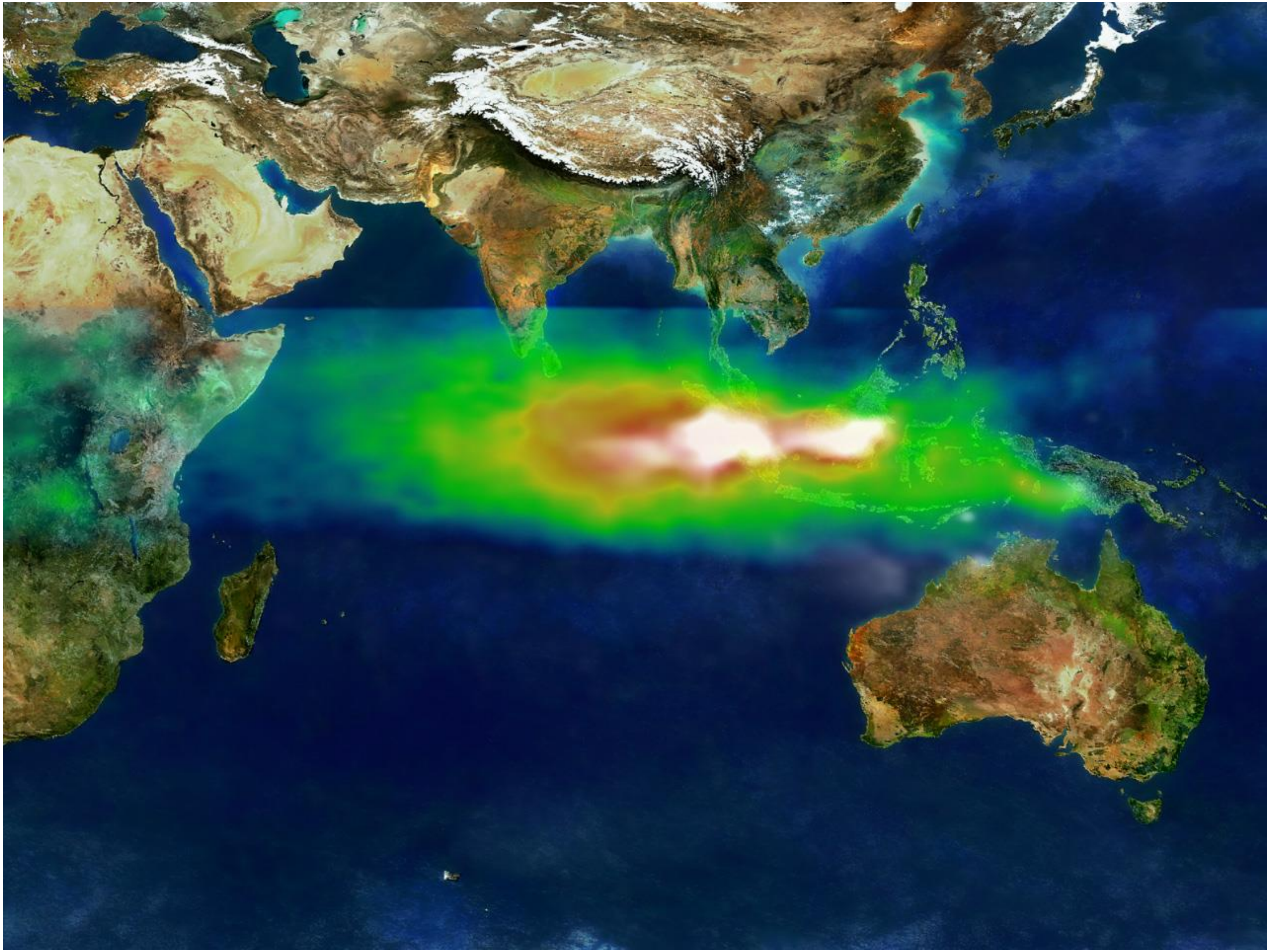


The Troposphere





Micro-
Scale
Urban or
Local Scale
Regional or
Mesoscale
Synoptic or
Global Scale
Long-lived
Species
CFC's
N_2O
CH_4
CH_3CCl_3
CH_3Br
Moderately Long-
Lived Species
CO
Aerosols
Trop O_3
SO_2
H_2O_2
NO_x
DMS
C_3H_6
C_5H_8
Short-lived
Species
CH_3O_2
HO_2
NO_3
OH
Inter-
Hemispheric
Mixing Time
Intra-
Hemispheric
Mixing Time
Boundary Layer
Mixing Time
Time Scale
100yrs
10yrs
1yr
1day
1hr
100s
1s
1m
10m
100m
1km
10km
100km
1000km
10,000km
Space Scale



Atmospheric Fate of Species

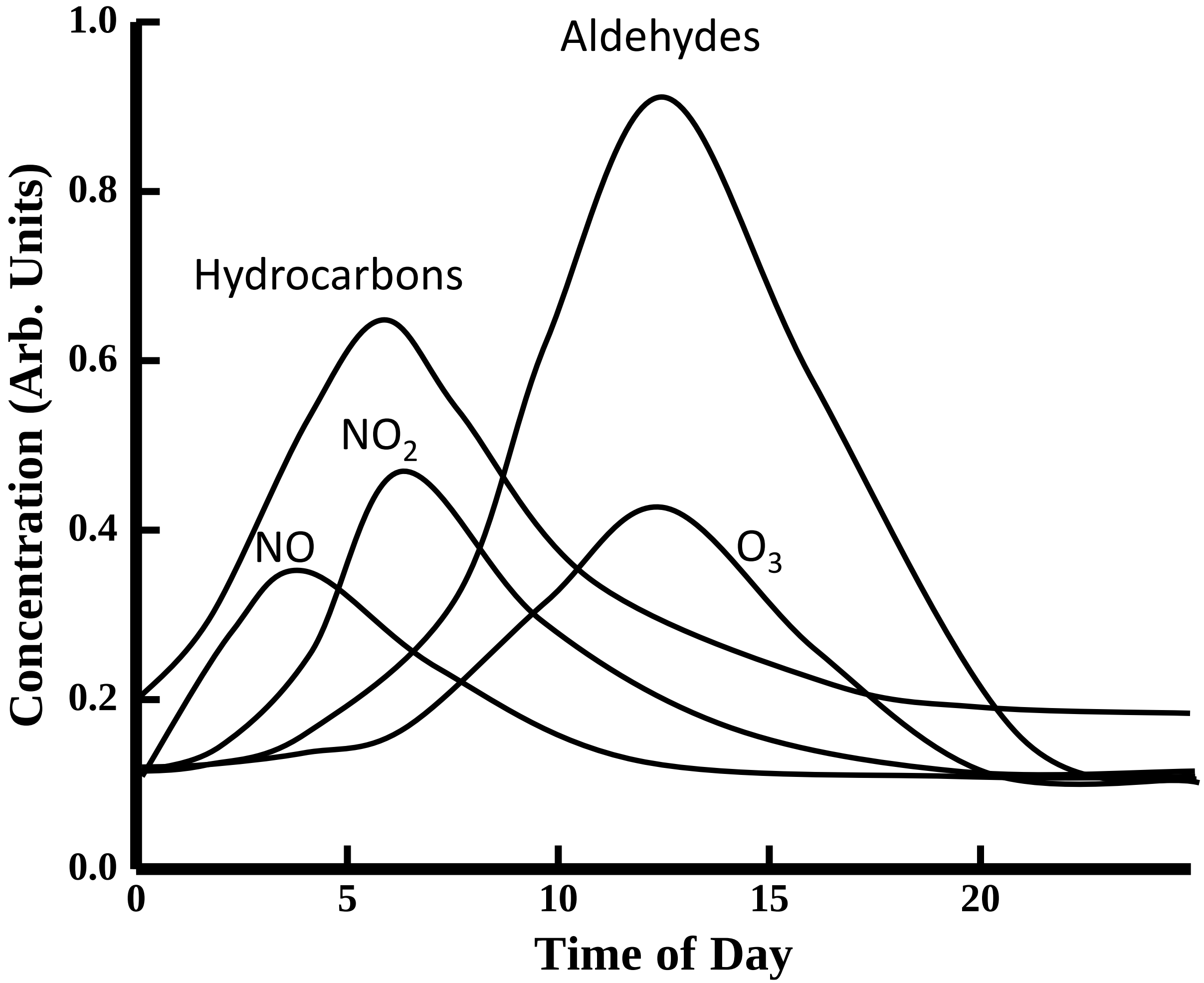
Water Soluble	$\xrightarrow{\text{yes}}$	Rain-out
Readily Photolyzed	$\xrightarrow{\text{yes}}$	Free Radicals
Multiple Bonds	$\xrightarrow{\text{yes}}$	Free Radicals
Labile Hydrogen	$\xrightarrow{\text{yes}}$	Free Radicals
Inert	$\xrightarrow{\text{yes}}$	Transported to Stratosphere

Tropospheric Ozone

Natural background due to Troposphere Stratosphere exchange is 20-60 ppb

Often observe Ozone levels >120 ppb near urban centers

Photochemical Smog Event



Photochemistry of O_3

$$O_3 + h\nu \rightarrow O(^3P) + O_2$$

ground state, unexcited, atoms

$$O(^3P) + O_2 \rightarrow O_3$$

recombination

The Formation of OH

$$O_3 + h\nu \rightarrow O(^1D) + O_2$$

excited atoms

90% $O(^1D) + N_2,O_2 \rightarrow O(^3P) + N_2,O_2$ 'quenching'

10% $O(^1D) + H_2O \rightarrow OH + OH$

The Formation of OH

$$-\frac{d[O(^1D)]}{dt} = k_r[H_2O][O(^1D)]$$

$$-\frac{d[O(^1D)]}{dt} = k_q[M][O(^1D)]$$

$$\frac{k_r[H_2O][O(^1D)]}{k_q[M][O(^1D)]} = \frac{k_r[H_2O]}{k_q[M]}$$

$$\frac{k_r[H_2O]}{k_q[M]} \approx 0.12$$

Photochemistry of O_3

Hartley Band

$$O_3 + h\nu \rightarrow O_2(^1\Delta_g) + O(^1D)$$

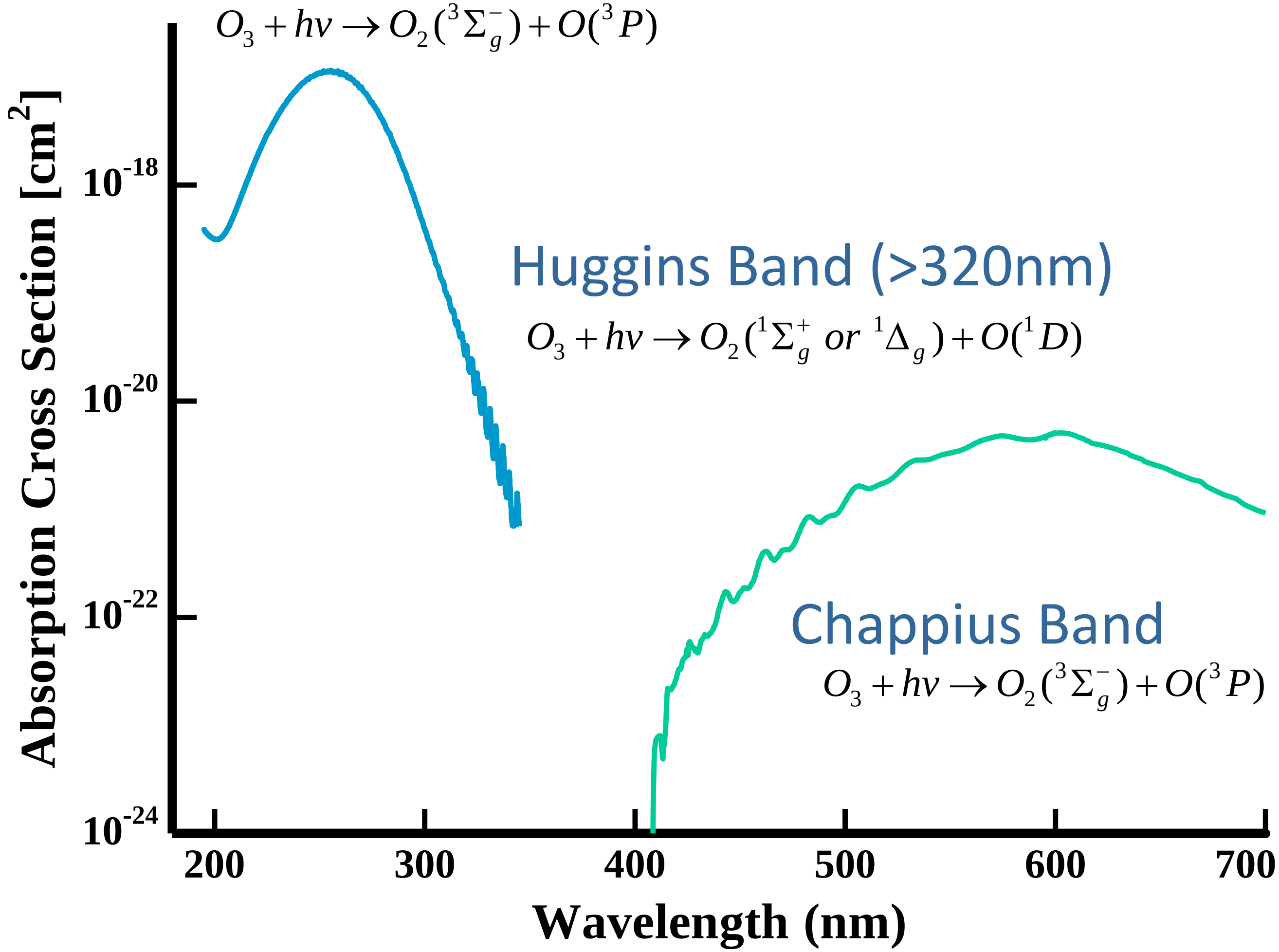
$$O_3 + h\nu \rightarrow O_2(^3\Sigma_g^-) + O(^3P)$$

Huggins Band (>320nm)

$$O_3 + h\nu \rightarrow O_2(^1\Sigma_g^+ \ or \ ^1\Delta_g) + O(^1D)$$

Chappius Band

$$O_3 + h\nu \rightarrow O_2(^3\Sigma_g^-) + O(^3P)$$



Quantum Yields

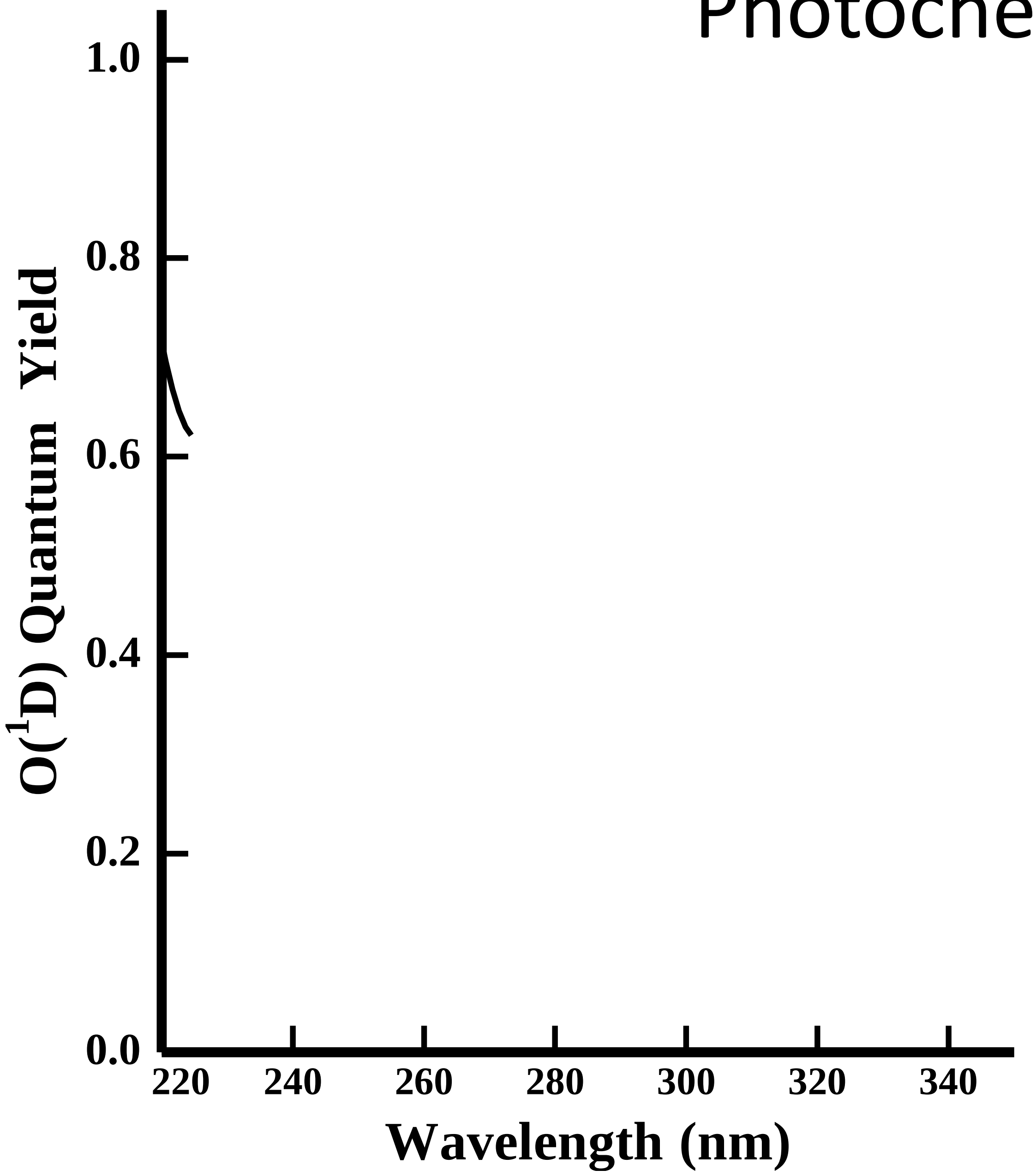
$$\phi_i = \frac{\#\,of\;\; excited\;\, molecules\;\, proceeding\;\, by\;\, process\; i}{total\;\#\,of\;\; photons\;\, absorbed}$$

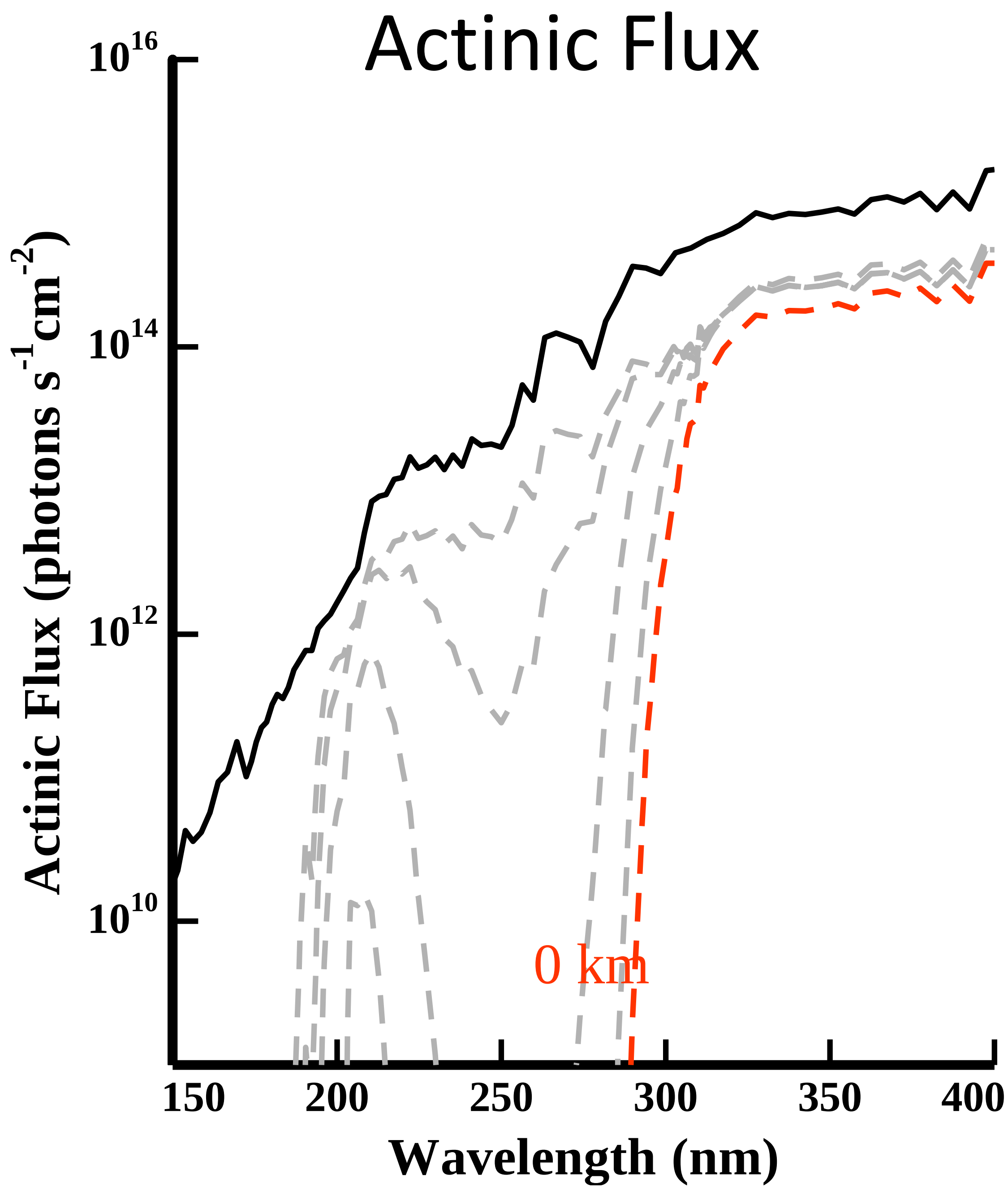
$$O_3 + h\nu \xrightarrow{a} O_2 + O(^3P)$$
$$O_3 + h\nu \xrightarrow{b} O_2 + O(^1D)$$

$$\phi_a = \frac{\#\,of\;\; O(^3P)\;\, atoms\;\; formed}{total\;\#\,of\;\; photons\;\, absorbed}$$

$$\sum_i \phi_i = 1.0$$

Photochemistry of O_3





Actinic Flux
10^{16}
10^{14}
10^{12}
10^{10}
Actinic Flux (photons $s^{-1} cm^{-2}$)
0 km
150
200
250
300
350
400
Wavelength (nm)

The Formation of OH

$$O_3 + h\nu \rightarrow O(^1D) + O_2$$

$$O(^1D) + H_2O \rightarrow OH + OH$$

Diurnal cycle

Average daytime concentration
[OH] ~ 1×10^6 molecules cm^{-3}

The Role of NOx

$N_2 + O_2 \rightarrow NO + NO$ combustion 2500 K

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

NO, NO_2 are referred to as NOx

The Role of NOx

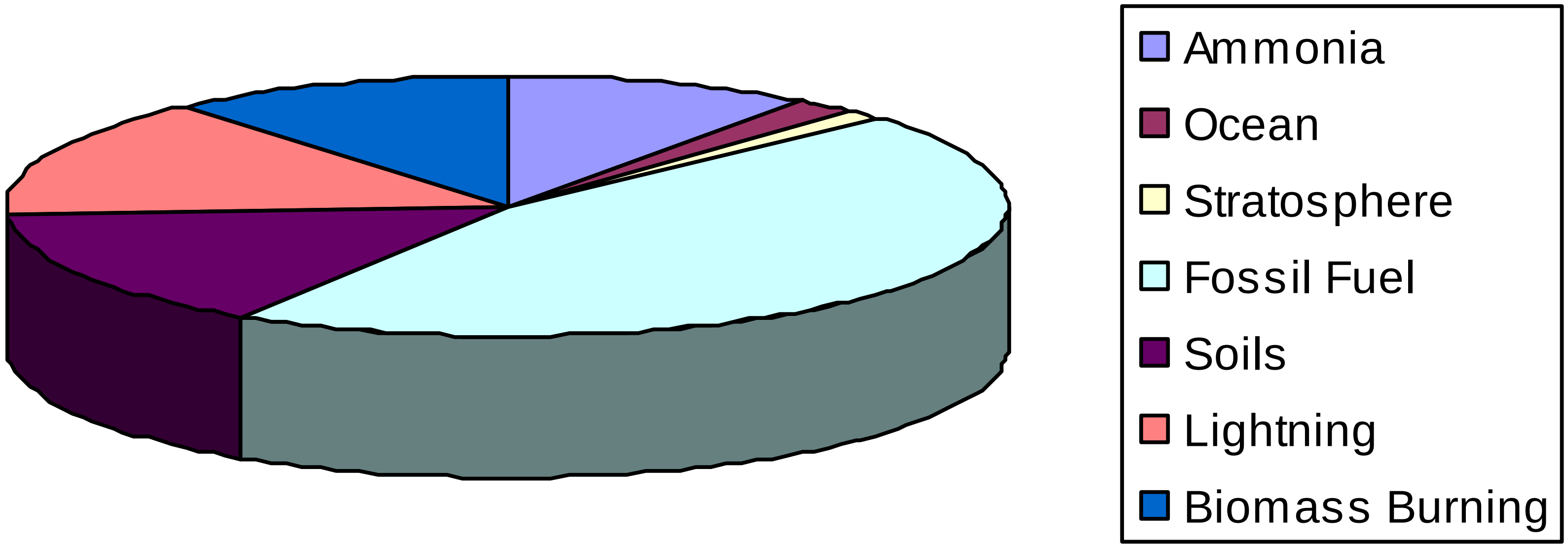
$$NO_2 + h\nu \rightarrow O(^3P) + NO$$

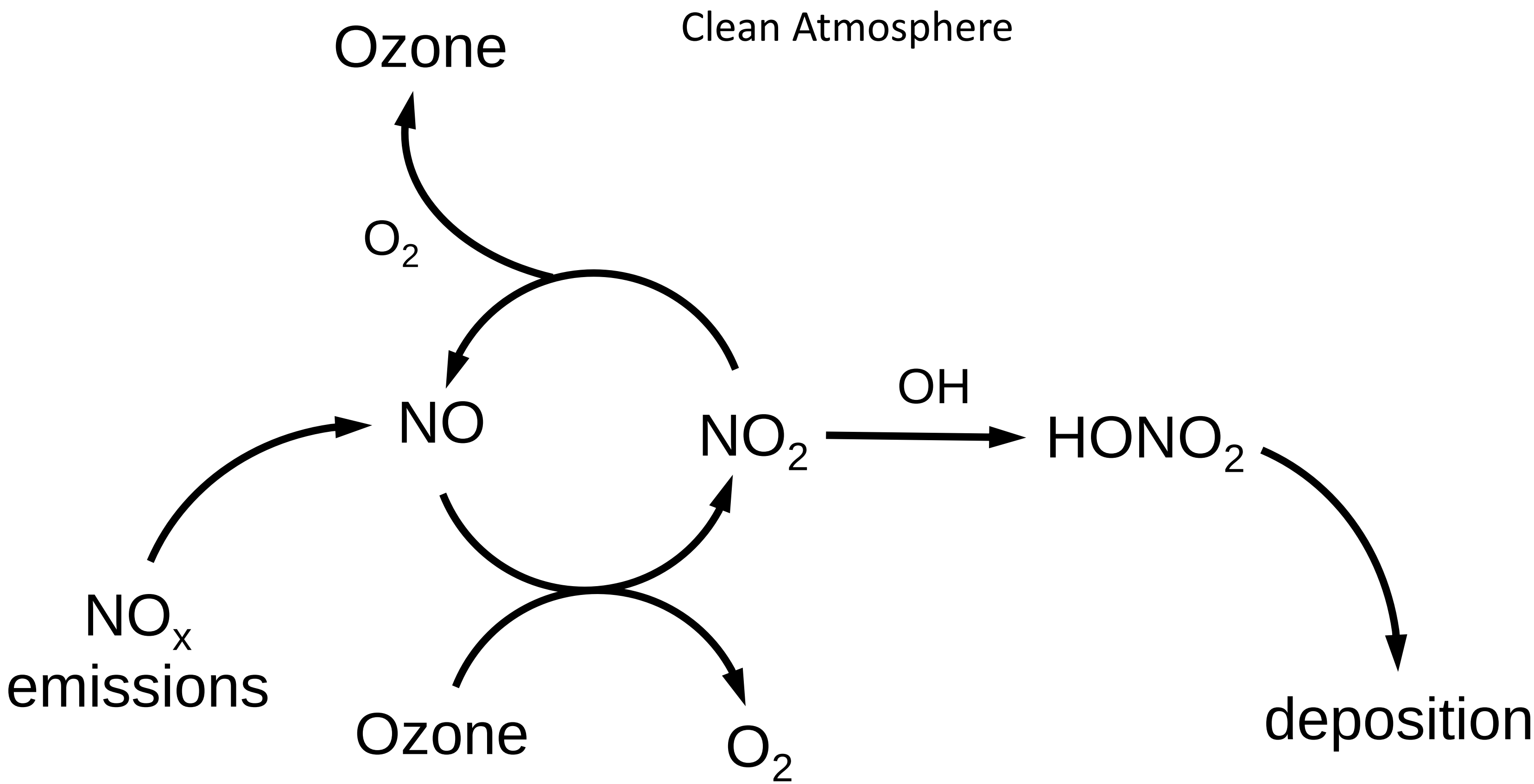
ground state atoms

$$O(^3P) + O_2 \rightarrow O_3$$

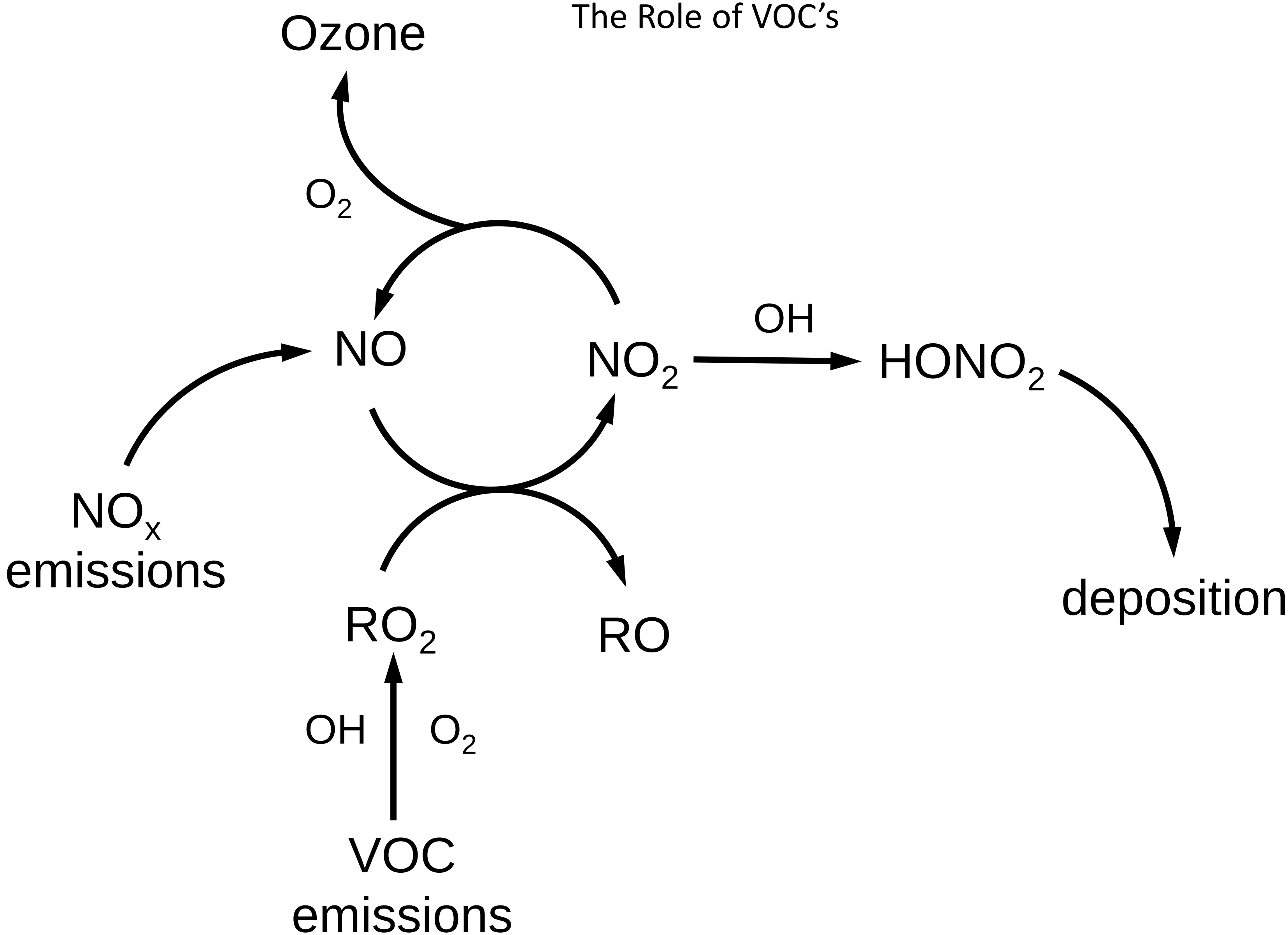
formation of O_3

Other Sources of NOx




Clean Atmosphere
Ozone
O_2
NO
NO_2
OH
$HONO_2$
NO_x emissions
Ozone
O_2
deposition

The Role of VOC’s



Hydrocarbon Oxidation -alkanes

$RH + OH \rightarrow R\bullet + H_2O$ 'hydrogen abstraction'

$R\bullet + O_2 \rightarrow RO_2\bullet$ 'dioxygen addition'

peroxy radicals

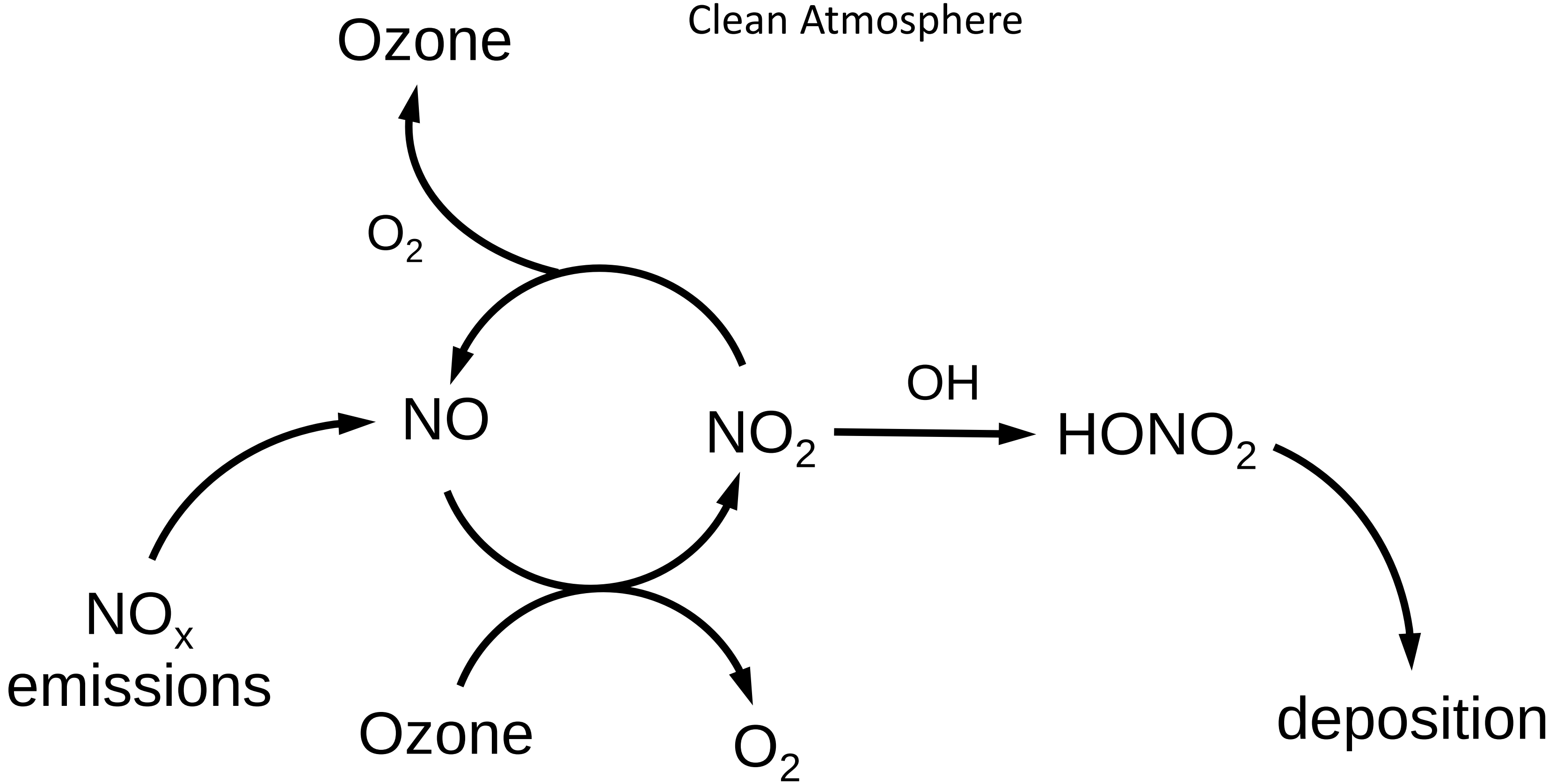
$RO_2\bullet + NO \rightarrow RO\bullet + NO_2$ 'oxygen abstraction'

Hydrocarbon Oxidation -alkanes

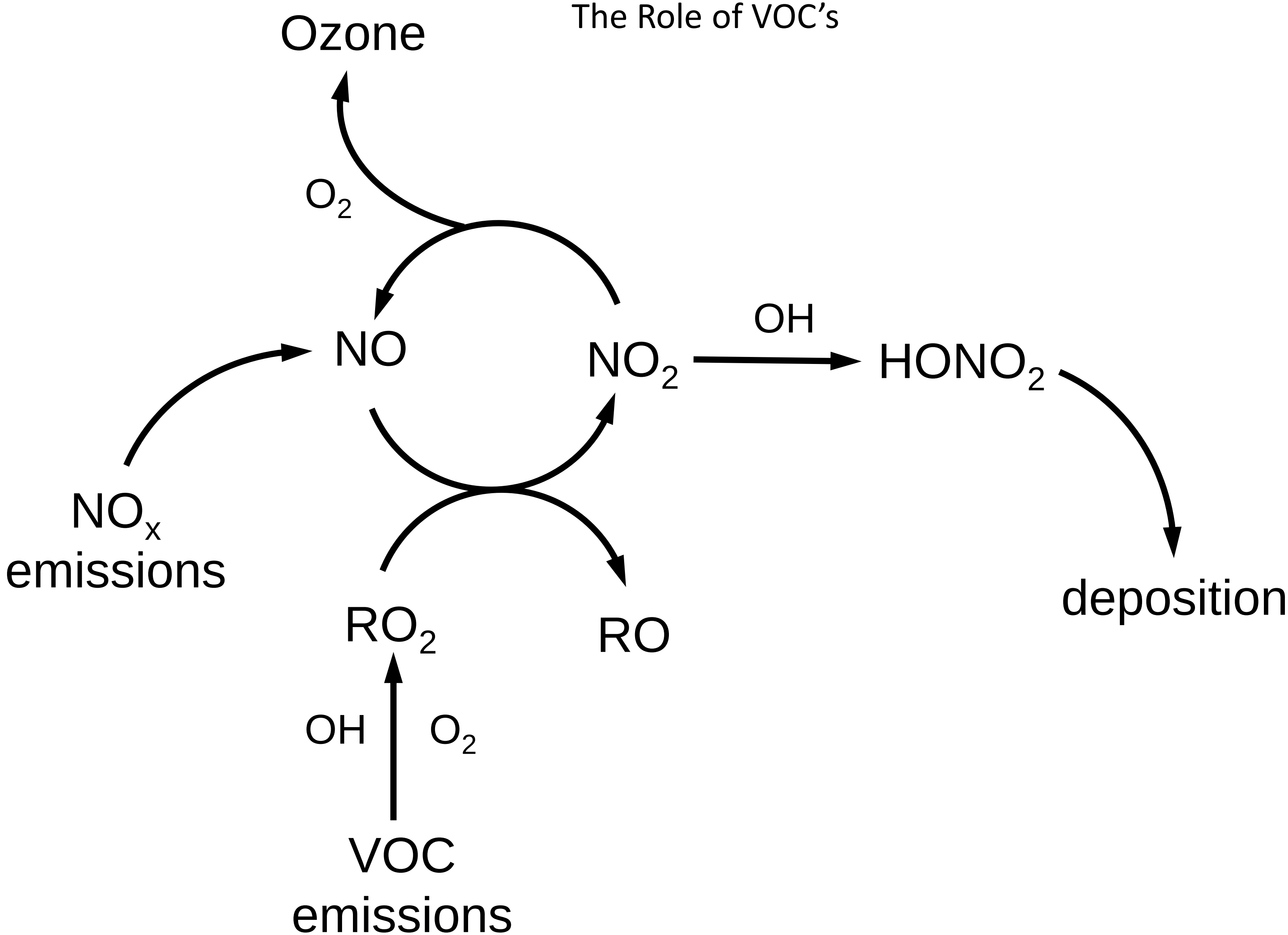
$RO\bullet + NO_2 \rightarrow RCHO + HOO\bullet$ ‘formation of aldehyde’

$HOO\bullet + NO \rightarrow NO_2 + OH\bullet$ ‘regeneration of NO_2’

Clean Atmosphere



The Role of VOC’s



Secondary Reactions:PAN Formation

$$CH_3CHO + OH\bullet \rightarrow CH_3CO\bullet + H_2O$$

$$CH_3CO\bullet + O_2 \rightarrow CH_3C(O)O_2\bullet$$ acetylperoxy

$$CH_3C(O)O_2\bullet + NO_2 \rightarrow CH_3C(O)OONO_2$$

peroxyacetic nitric anhydride (PAN)

Photochemical Smog

Species	Concentration $\mu g\ m^{-3}$ Polluted Areas	Unpolluted Areas
CO	10,000-30,000	<200
NO_2	100-400	<20
Hydrocarbons (not Methane)	600-3,000	<300
Ozone	50-150	<5
PANs	50-250	<5

VOCs in Taipei City

Species	Concentration $\mu g\ m^{-3}$
Toluene	980
m,p-xylene	910
Benzene	370
Ethylbenzene	310
Hexane	150
Heptane	130

Methane Oxidation

$$CH_4 + OH\bullet \rightarrow CH_3\bullet + H_2O$$

$$CH_3\bullet + O_2 \rightarrow CH_3O_2\bullet$$

$$CH_3O_2\bullet + NO \rightarrow CH_3O\bullet + NO_2$$

$$CH_3O\bullet + O_2 \rightarrow CH_2O + HO_2$$

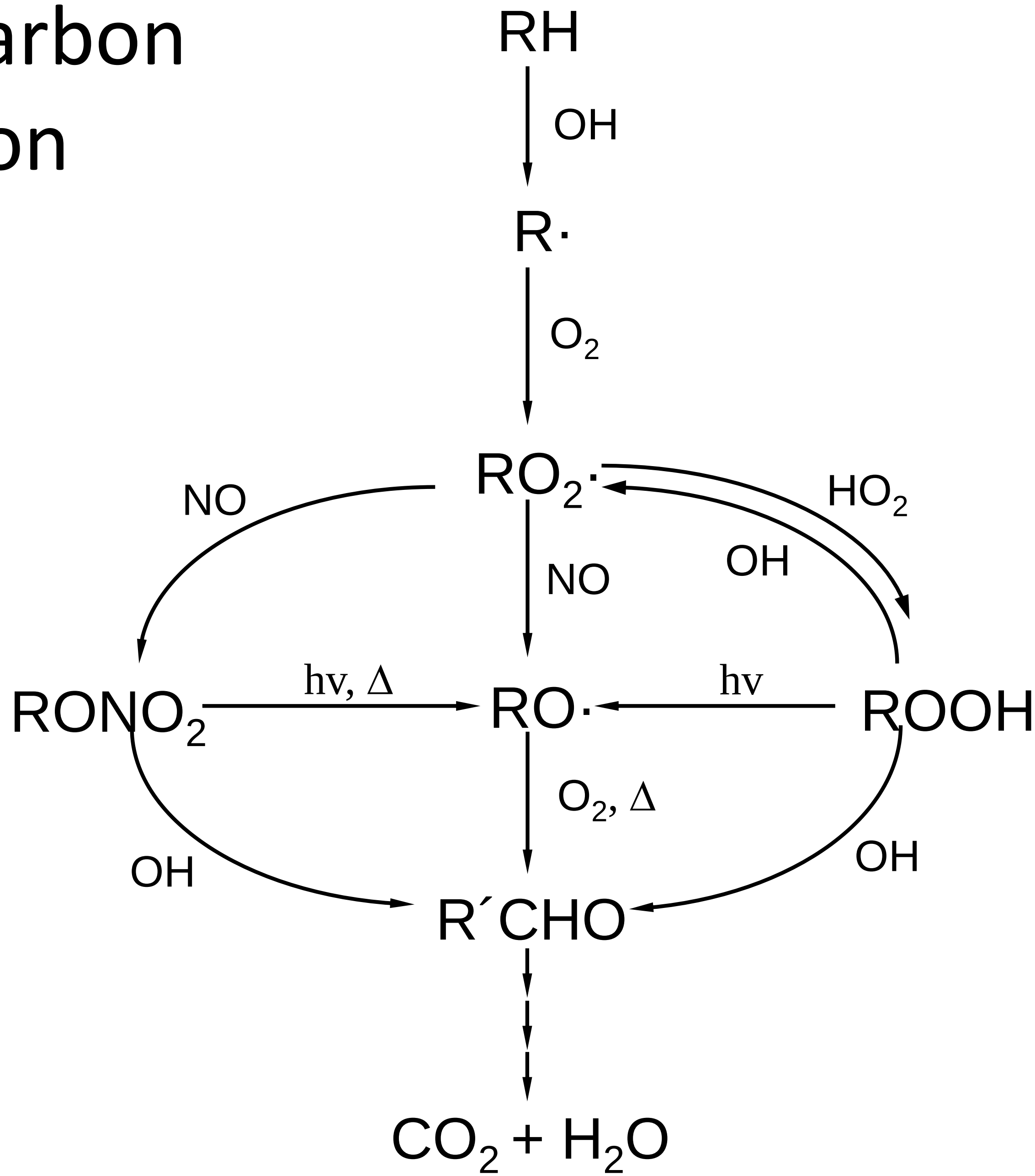
Formaldehyde Photolysis

$CH_2O + h\nu\ (\lambda < 330\ nm) \rightarrow HCO\bullet + H\bullet$

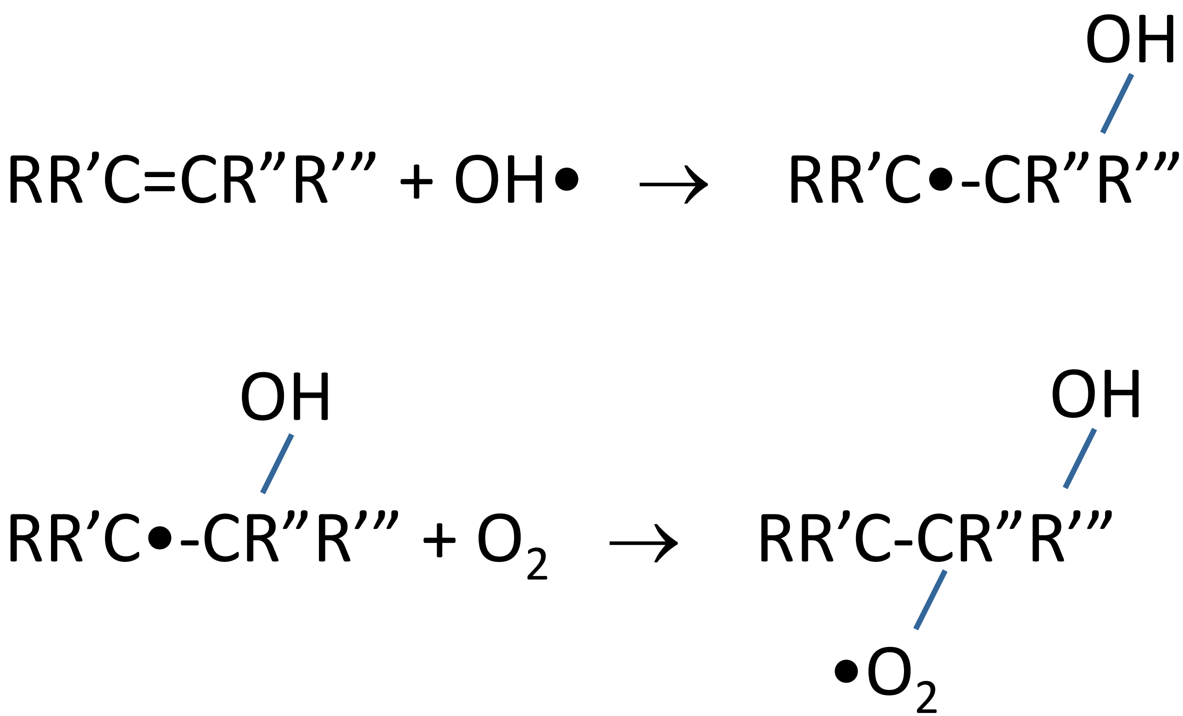
$HCO\bullet + O_2 \rightarrow HO_2\bullet + CO$

$CO + HO\bullet \rightarrow CO_2 + H\bullet$

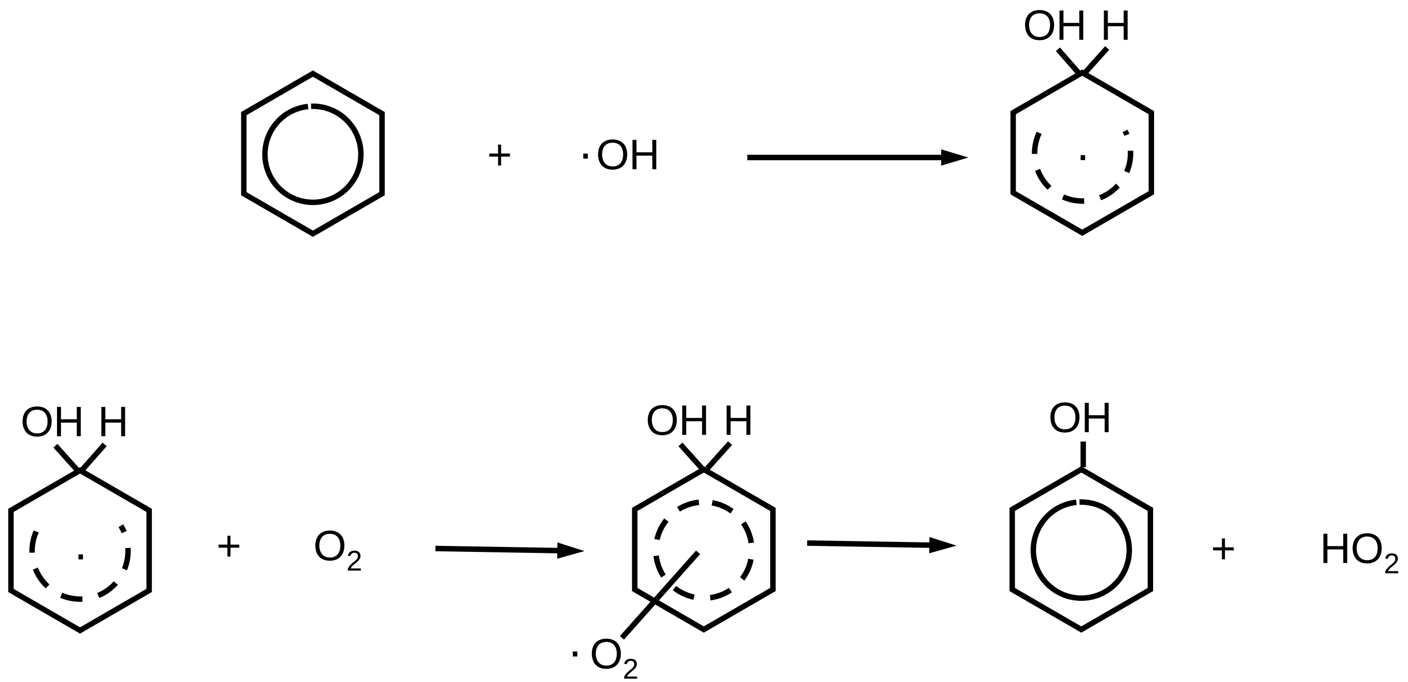
Hydrocarbon Oxidation



Alkene Oxidation



Aromatic Oxidation



Tropospheric Chemistry:

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Primary vs. Secondary Air Pollutants:

- Primary pollutants: released directly from sources. Ex. CO, SO_2, NO_x
- Secondary pollutants: formed through chemical reactions of the primary pollutants. Ex. O_3

$HO_2\bullet$ Radical: Interconversion of OH • and $HO_2\bullet$

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

$$OH\bullet + RCH_3 \rightarrow H_2O + RCH_2\bullet$$

$$RCH_2\bullet + O_2 \rightarrow RCH_2OO\bullet$$

$$RCH_2OO\bullet + NO \rightarrow NO_2 + RCH_2O\bullet$$

$$RCH_2O\bullet + O_2 \rightarrow RCHO + HO_2\bullet$$

Half-life for Reaction with OH and NO_3

Molecule	OH	NO_3
n-butane	5 days	205 days
acetylene	14 days	188 days
toluene	2 days	138 days
formaldehyde	1.2 days	16 days

NO_3 reaction rates 10^{-6} - 10^{-18} cm^3s^{-1}

OH reaction rates 10^{-13} cm^3s^{-1}

Reduce Hydrocarbon Emission or Reduce Nox Emissions?

“Control Strategies”

Number of Days Exceeding the Ozone Standard 1984-1990

	1984	1985	1986	1987	1988	1989	1990
Dallas/Fort Worth	19	18	11	11	9	4	7
Tyler/Longview	1	1	0	0	0	0	2
El Paso	8	10	11	12	6	10	4
Beaumont/ Port Arthur	13	0	8	3	7	9	5
Houston/Brazoria/ Galveston	56	58	48	54	59	37	52
San Antonio	1	0	1	1	1	0	0
Austin	0	2	0	0	0	0	0
Corpus Christi	1	0	0	2	0	0	1

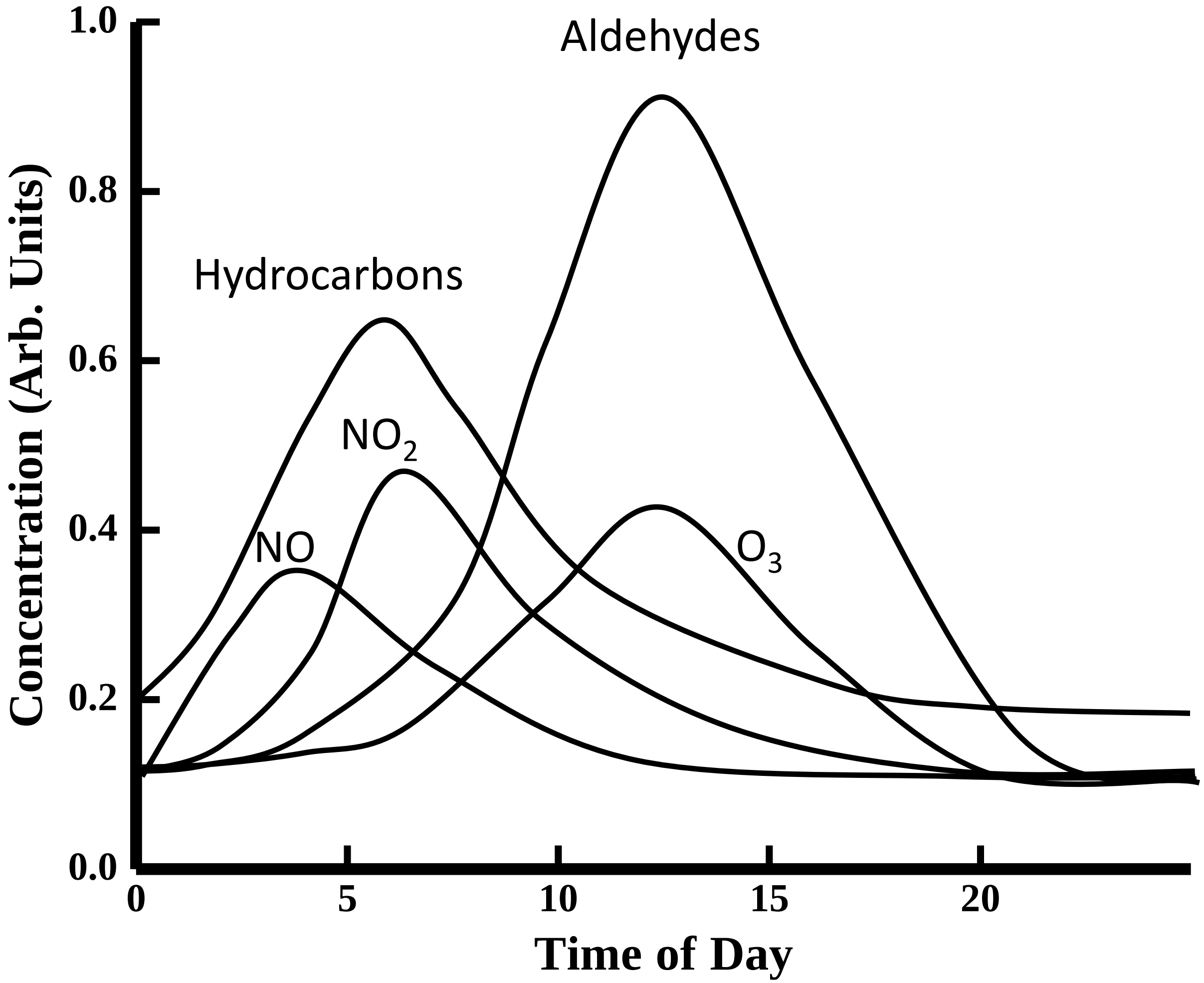
Note: Totals include only state and local governmental ozone monitoring sites, not private networks. Source: Texas Natural Resource Conservation Commission, Data Management and Analysis Division, 1995.

Control Strategies for Ozone

- Control of VOCs
  - General too abundant to be brought low enough to be the limiting factor.
  - In certain areas, VOCs from biological sources could be significant.

- Control of NOx
  - Difficult to control as efficient energy conversion requires high combustion temperature.

Photochemical Smog Event



NATIONAL AMBIENT AIR QUALITY STANDARDS (NAAQS)

POLLUTANT	AVERAGING PERIOD	PRIMARY NAAQS	NOTES
Ozone	1-Hour	0.125 ppm	
	8-Hour	0.085 ppm	
Carbon Monoxide	1-Hour	35.50 ppm	
	8-Hour	9.50 ppm	
Sulfur Dioxide	Annual	0.03 ppm	
	24-Hour	0.14 ppm	
Nitrogen Dioxide	Annual	0.053 ppm	
Respirable Particulate Matter	24-Hour	155.00 $\mu g/m^3$	
(PM10)	Annual	51.00 $\mu g/m^3$	
Lead	Quarter	1.55 $\mu g/m^3$	

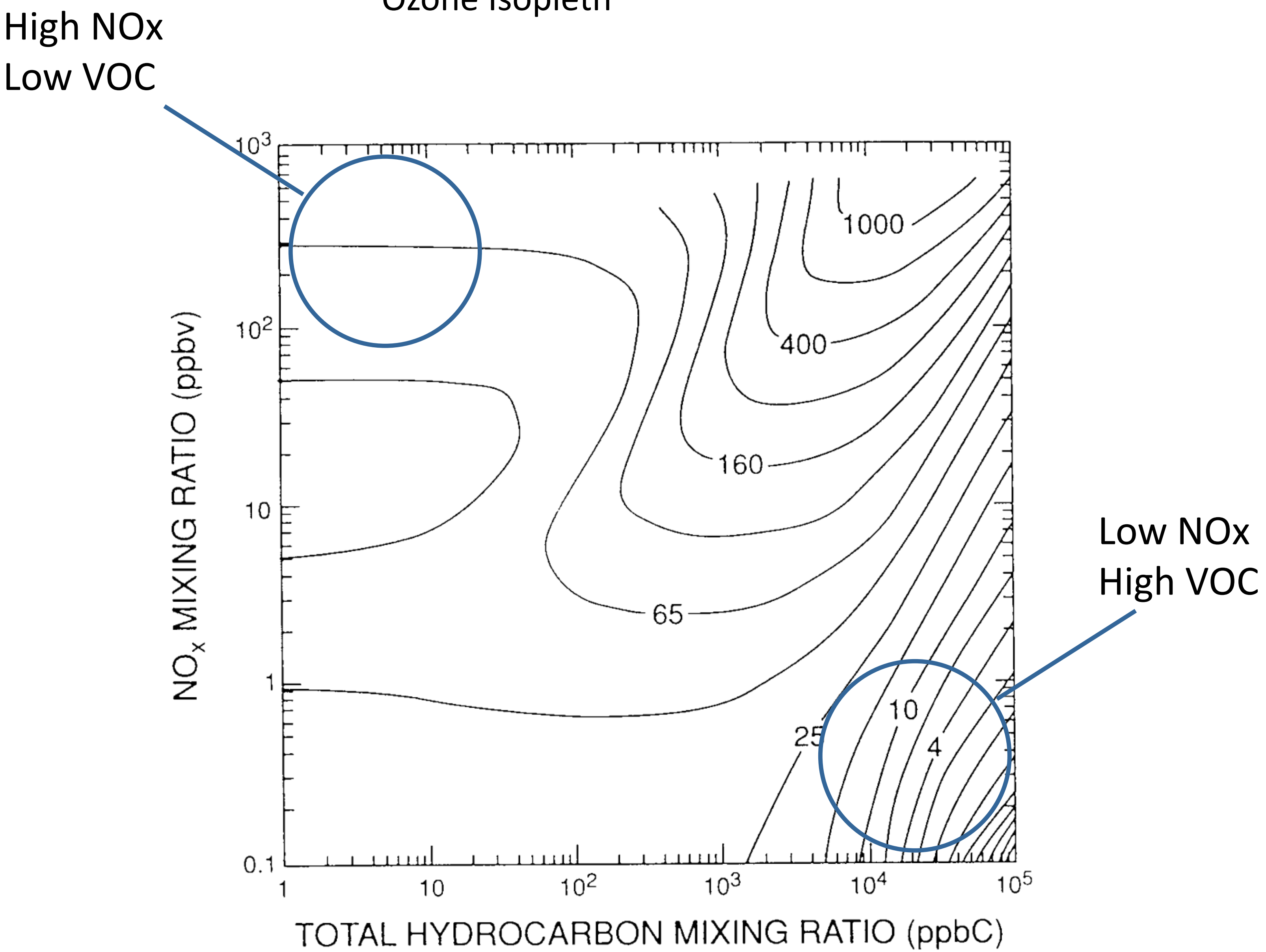
Source: Texas Air Control Board, Texas Air Control Board Fact Sheets: National Ambient Air Quality Standards (Austin: TACB, 1993), 3.

1992 AIR EMISSION OF TOXICS IN MILLIONS OF POUNDS IN TEXAS, SELECTED STATES AND THE U.S.

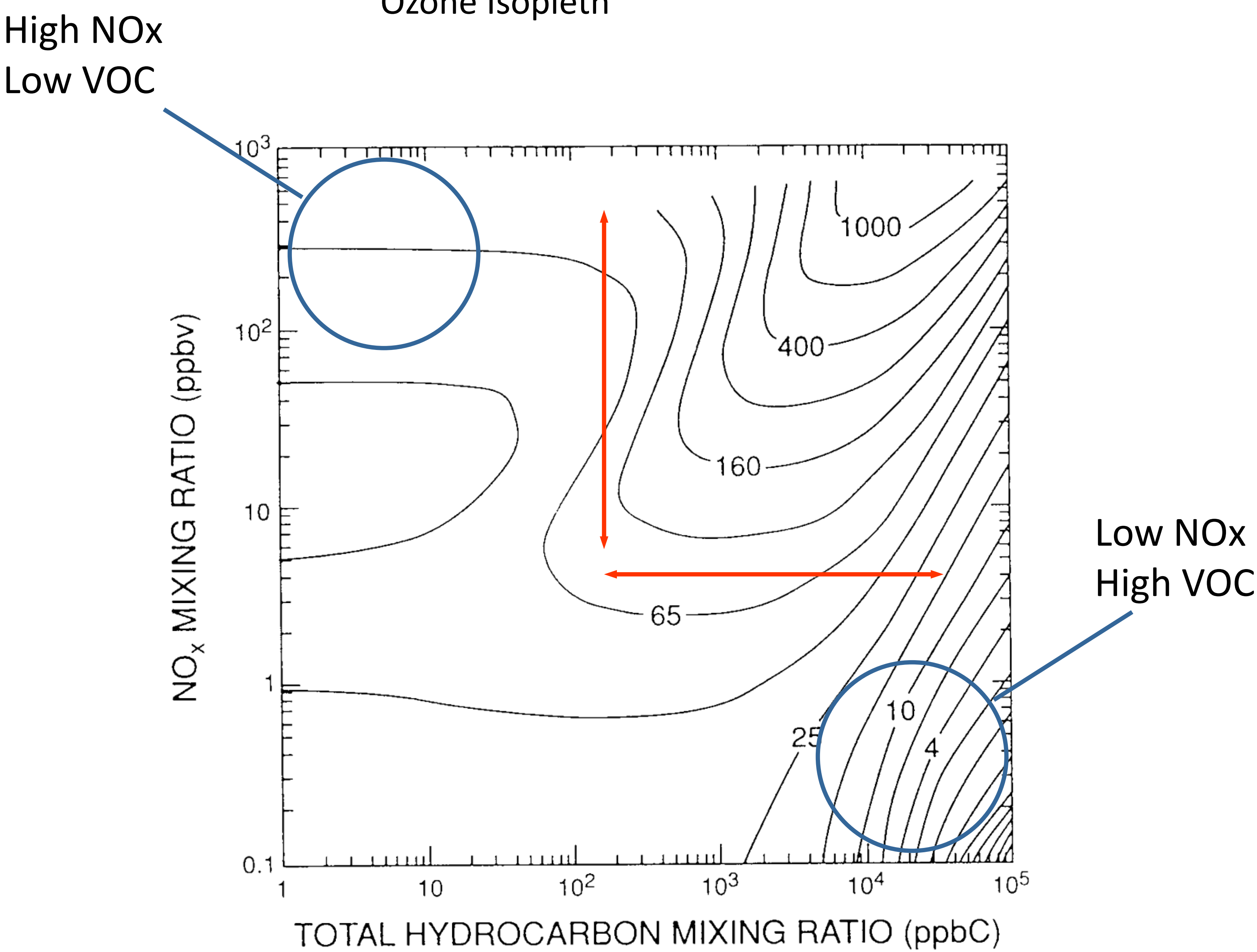
	FUGITIVE AIR EMISSIONS	POINT AIR EMISSIONS	TOTAL
Texas	76.1	81.3	157.5
Tennessee	35.8	91.5	127.4
Alabama	14.8	80.2	94.9
Ohio	28.2	62.5	90.7
Louisiana	21.5	67.5	89.1
Indiana	28.1	57.9	85.9
Top Six States	**205**	**441**	**646**
Wyoming	0.9	1.4	2.3
New Mexico	0.5	1.5	2.0
North Dakota	0.5	1.3	1.8
Nevada	0.4	0.5	0.9
Vermont	0.3	0.5	0.8
Hawaii	0.4	0.1	0.6
Bottom Six	**3.0**	**5.3**	**8.4**
TOTAL U.S.	**549.4**	**1,295.6**	**1,845**

Source: Environmental Protection Agency, 1992 Toxics Release Inventory: Public Data Release (Washington, DC: U.S. Governmental Printing Office, May 1994), Table 1-6.

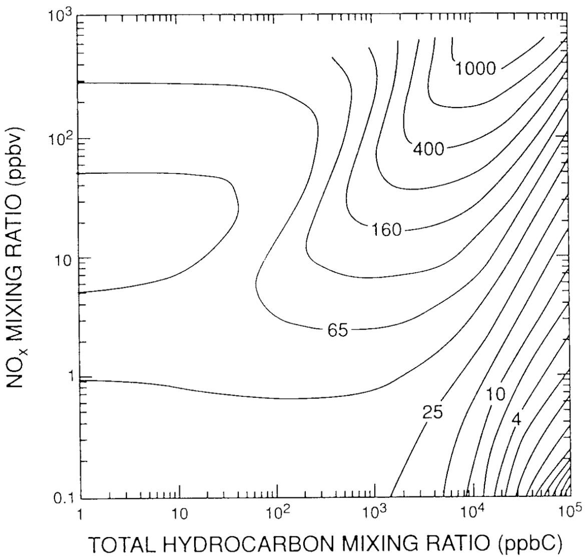
Ozone Isopleth



Ozone Isopleth



Ozone Isopleth



Does not include transport

Does not include ozone production from previous days

Does not include natural sources of hydrocarbons (NMOC)

Kill Trees or Reduce NOx?: Reducing Ground Level Ozone

Biogenic Non-Methane Organic Compounds (NMOC) Emissions

- Estimated 1150 Tg of carbon yr^{-1} from biogenic NMOCs is emitted worldwide

- NMOC emissions are ~10 times higher than anthropogenic NMOC emissions worldwide (~1.5 in North America)

Impact of Biogenic (non-methane,NMOC) Oxidation

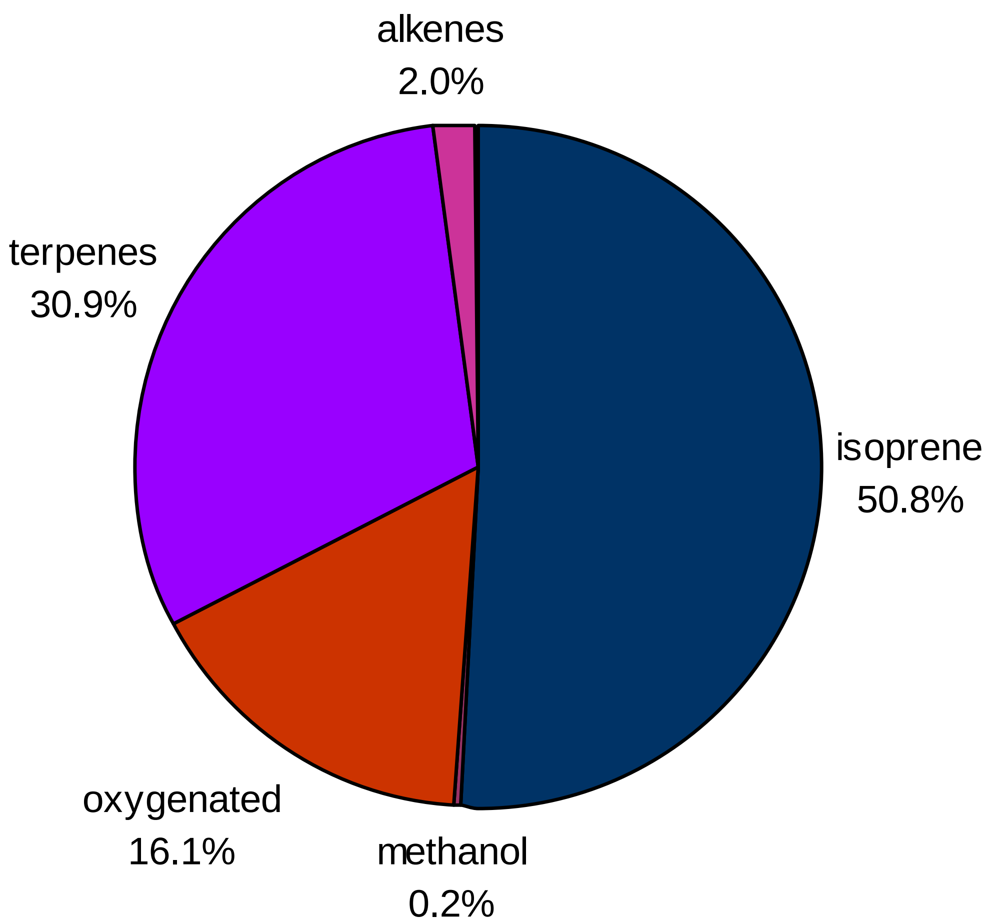
- The contribution of NMOC oxidation to tropospheric O_3 formation is estimated to be approximately 75% in parts of the US
- Oxidation of natural hydrocarbons contributes ~20% of the global CO budget
- A significant contribution of submicron aerosol mass is organic matter of biogenic origin

Biogenic NMOC		Lifetime[a] for reaction with OH	NO_3	O_3
isoprene		1.4 hr	50 min	1.3 day
camphene		2.6 hr	50 min	18 day
3-carene		1.6 hr	4 min	11 hr
limonene		50 min	3 min	2.0 hr
myrcene		40 min	3 min	50 min
α-pinene		2.6 hr	5 min	4.6 hr
β-pinene		1.8 hr	13 min	1.1 day
sabinene		1.2 hr	3 min	4.6 hr
β-caryophyllene		40 min	2 min	2 min
longifolene	3.0 hr	50 min	>33 day	
methanol		12 day	1 yr	>4.5 yr
2-methyl-3-buten-2-ol		2.1 hr	4 day	1.7 day
cis-3-hexen-1-ol		1.3 hr	2.1 hr	6 hr
linalool		50 min	3 min	55 min
1,8-cineole		1.0 day	270 day	>4.5 yr
cis-3-hexenylacetate		1.8 hr	2.3 hr	7 hr
6-methyl-5-hepten-2-one	55 min	4 min	1.0 hr	
methyl vinyl ketone		6.8 hr	>1.0 yr	3.6 day
methacrolein		4.1 hr	14 day	15 day
3-methylfuran		1.5 hr	3 min	19 hr
pinonaldehyde		2.9 hr	2.3 day	>2.3 yr
caronaldehyde		2.9 hr	1.9 day	>2.3 yr
sabinaketone		2.3 day	130 day	>0.9 yr
nopinone		10 hr	----	----
camphenilone		2.3 day	----	----

[a]With concentrations (molecule cm^{-3}) of: OH, 12-hr daytime average of 2.0×10^6; NO_3, 12-hr nighttime average of 5×10^8; O_3, 24-hr average of 7×10^{11}.

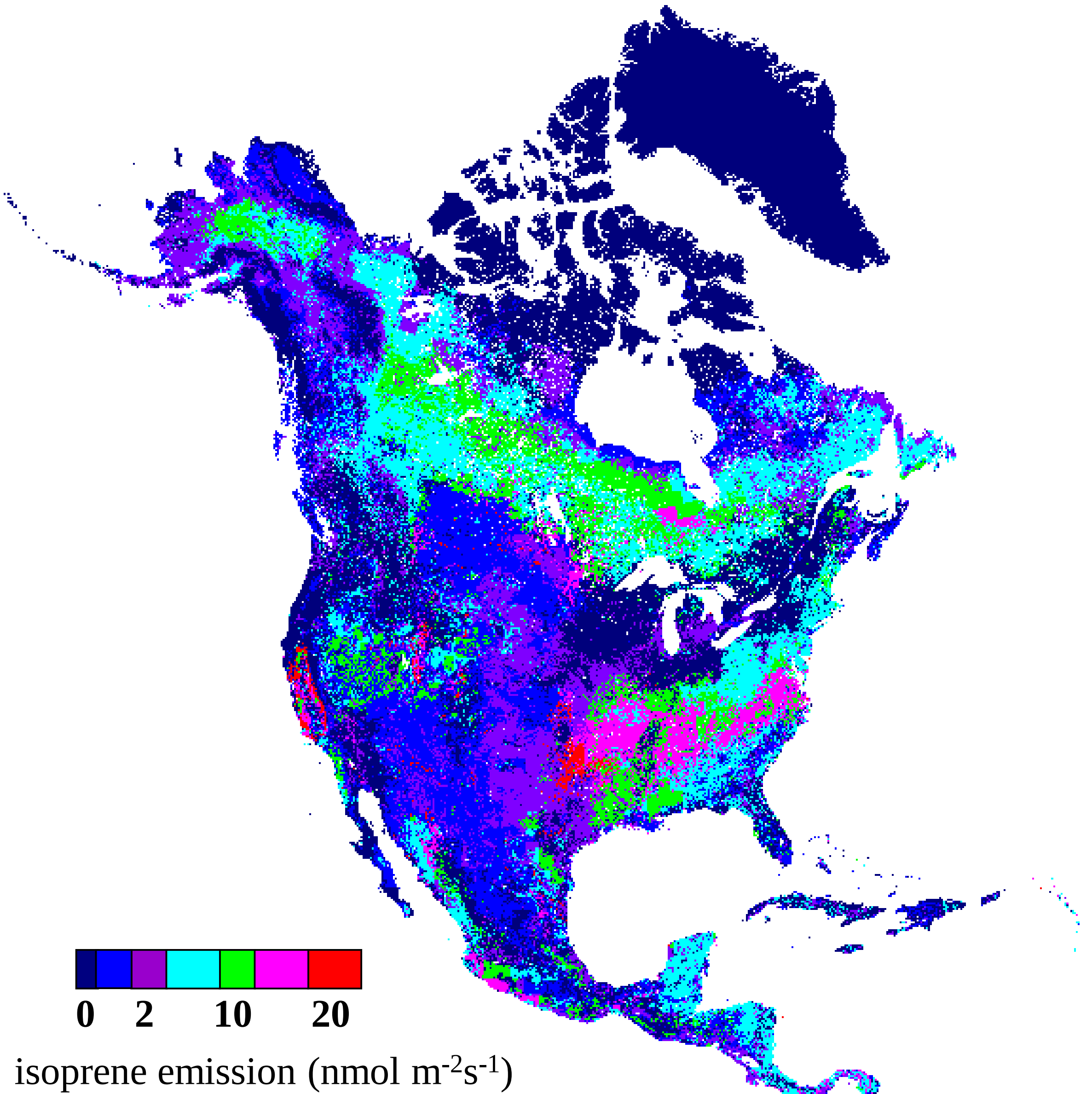
CH_4 lifetime: 10 years

Abundance of Biogenic NMOCs Emissions

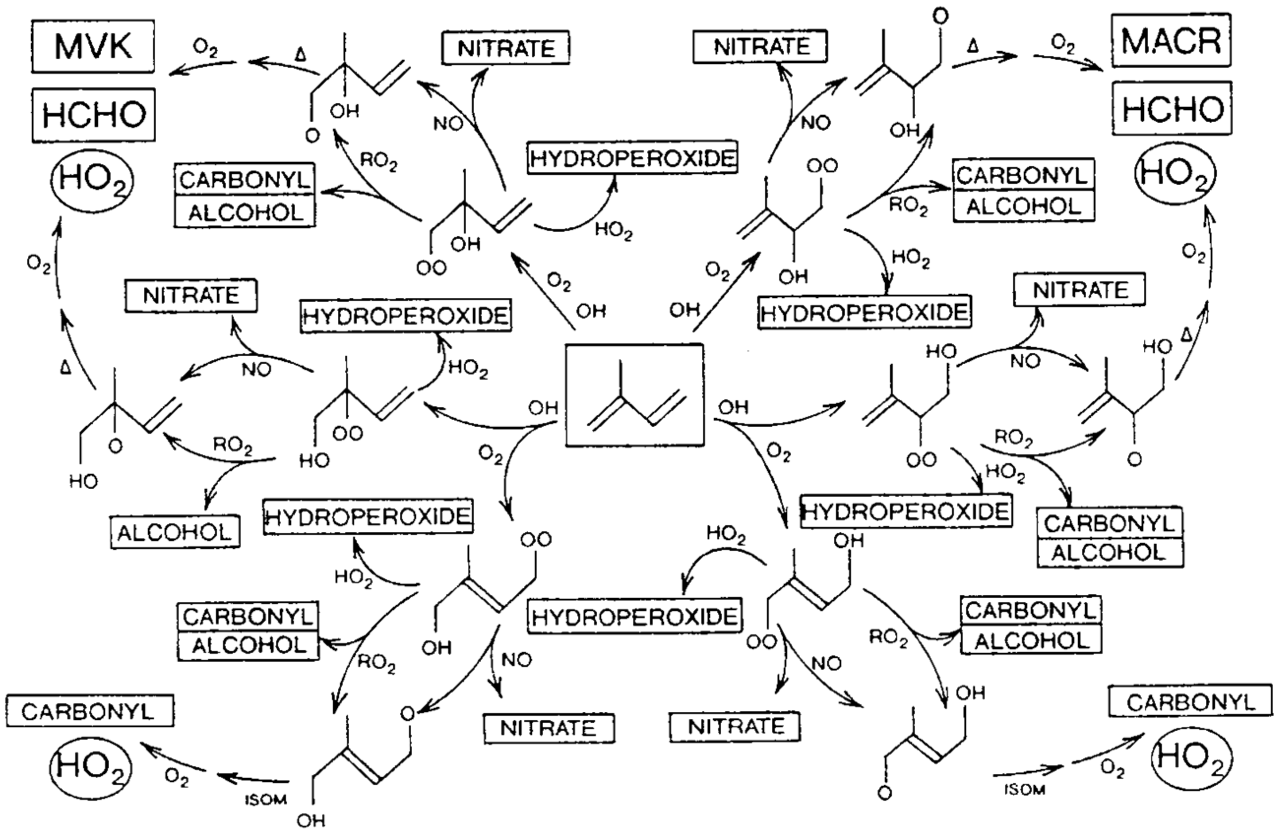


North American Continetial Biogenic NMOC Emissions weighted by OH Reactivity

North American Isoprene Emission



Isoprene Oxidation



The distribution of first generation products has been identified by numerous environmental chamber studies