Atmospheric Chemistry and Processes

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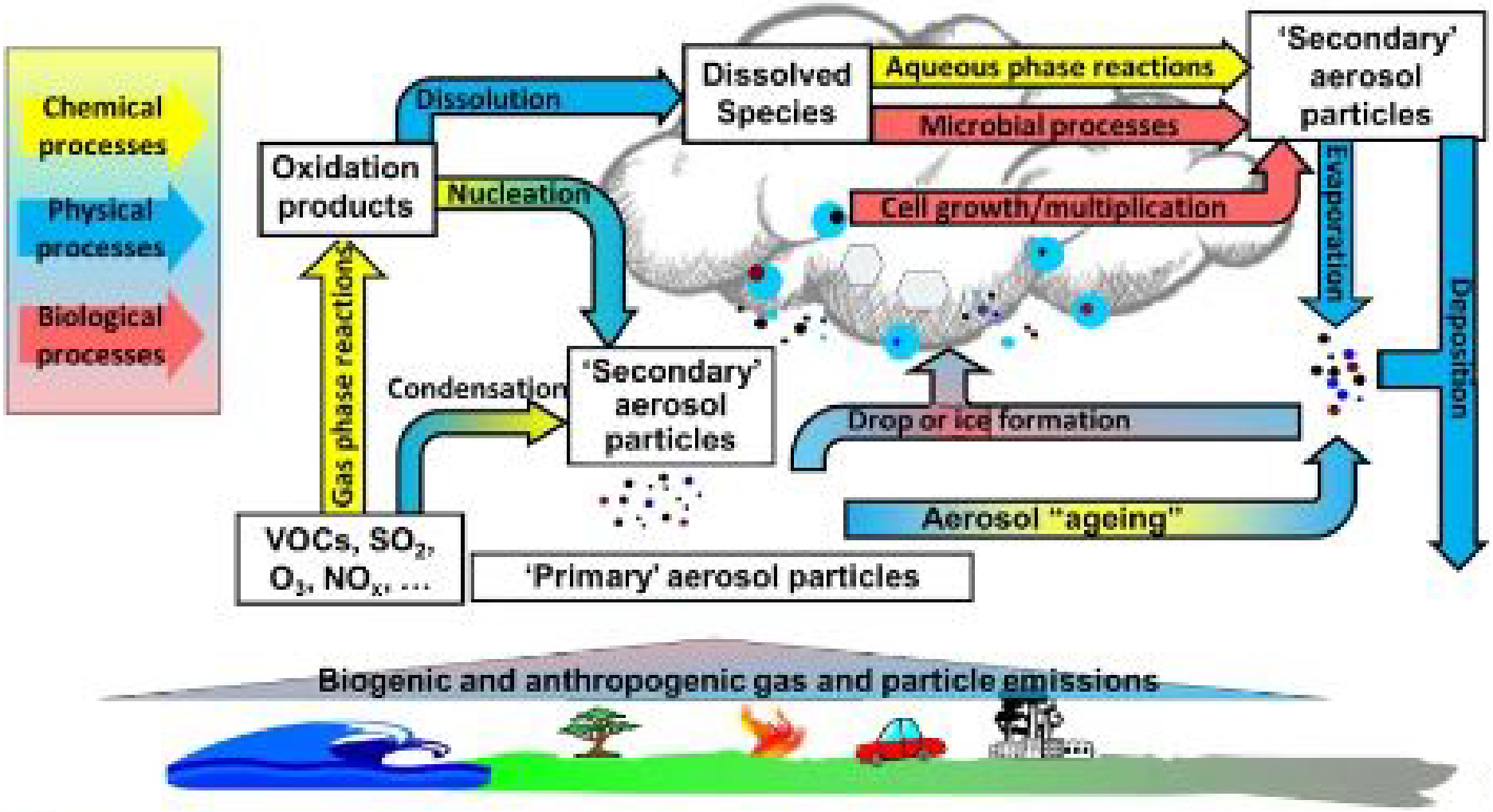
Outline

- **Atmospheric Processes**
  - Importance and Overview
  - Impact of Meteorology on Air Pollutants
  - Major Challenges in Air Pollution Meteorological Modeling
- **Atmospheric Chemistry**
  - Importance and Overview
  - Tropospheric Background and Urban Chemistry
  - Gas-phase Chemical Mechanisms used in Air Quality Models
  - Major Issues In O_3 and $PM_{2.5}$ Pollution Control
- **Summary**

Major sources: Jacobson (2012), Seinfeld and Pandis (2016), Seaman (2000), Zhang and Baklanov (2019), and Zhang (2015) and (2024)

The Atmosphere: An Interdisciplinary Lab (Ervens, 2021)



Atmospheric chemistry

- Chemical reactions in the gas, aqueous and particle phases

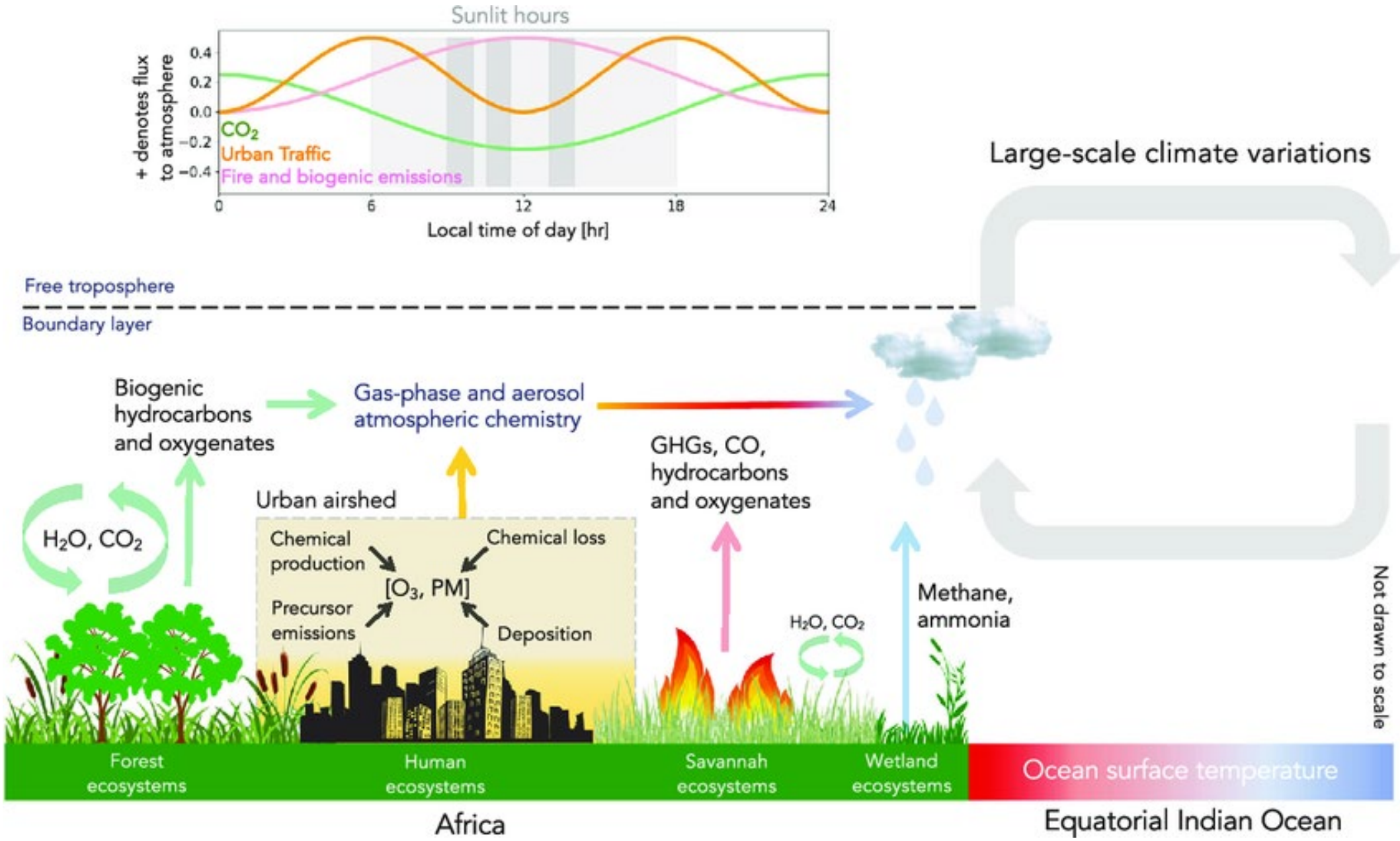
Atmospheric physics

- Physical processes, e.g. radiation, thermodynamic processes leading to warming, cloud formation etc

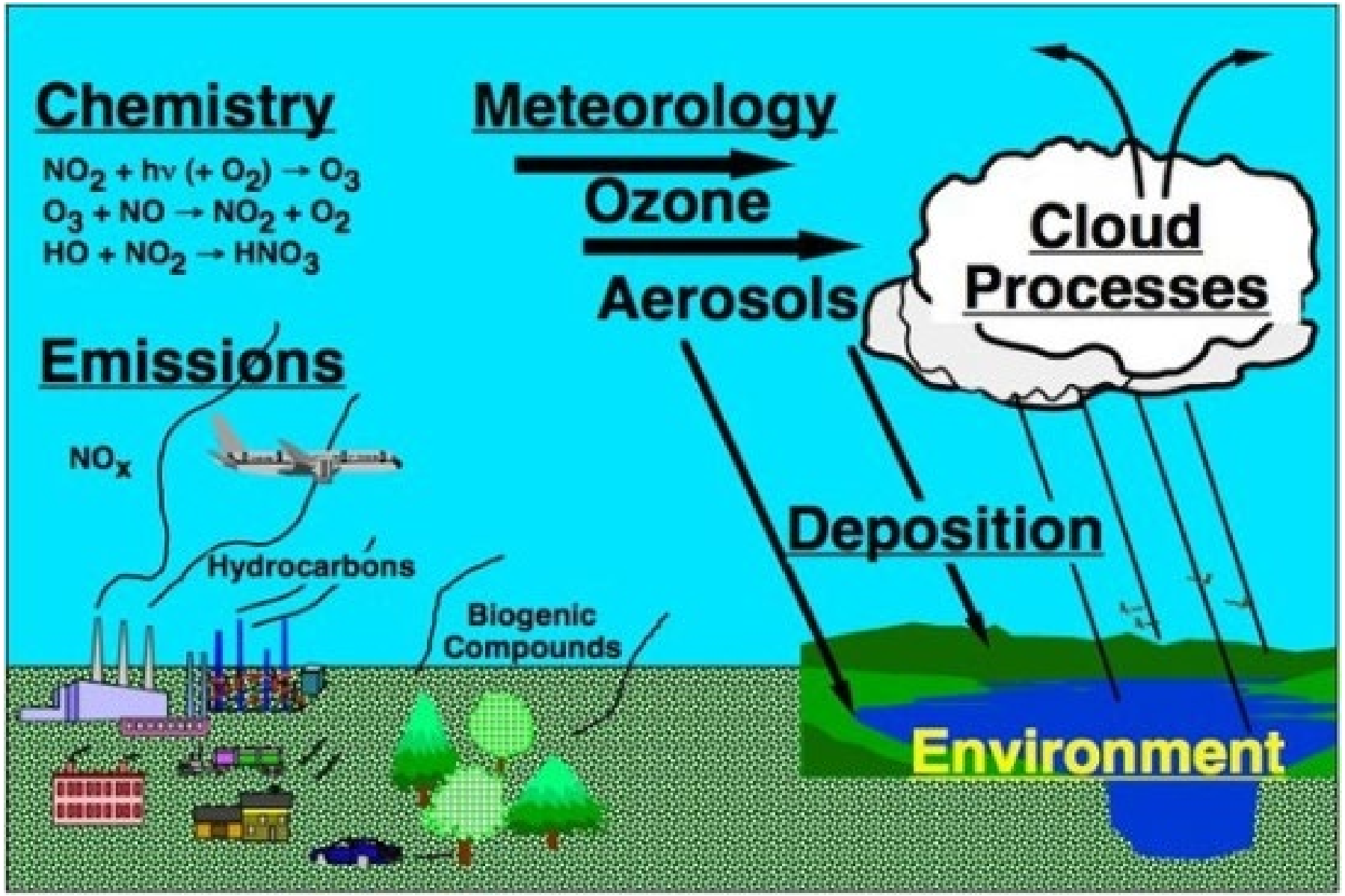
Atmospheric biology

- Interactions of microorganisms with chemical compounds
- Modification of microorganisms by chemical, physical and biological processes ....

Atmospheric processes that affect GHGs and atmospheric chemistry over the tropics (Palmer et al., 2022)



Overview of Major Atmospheric Processes Affecting Air Quality (Stockwell et al., 2012)



Science Components in an Atmospheric Model (Jacobson, 2005, Fig. 1.1)

- **Gas processes**
  - Emission
  - Photochemistry
  - Gas-to-particle conversion
  - Cloud removal
- **Aerosol processes**
  - Emission
  - Nucleation/condensation
  - Aerosol, cloud coagulation
  - Dissolution/chemistry/crystallization
  - Dry deposition/sedimentation
  - Rainout/washout
- **Cloud processes**
  - Activation on aerosol
  - Conden./evap./deposition/sublim.
  - Hom./het./contact/evap. freezing
  - Cloud, aerosol coagulation
  - Precipitation/lightning
  - Dissolution/chemistry
- **Radiative transfer**
  - UV/visible/near-IR/thermal-IR
  - Scattering/absorption
    Gas Aerosol Hydrometeor
  - Snow, ice, water albedos
  - Visibility
  - Heating rates
  - Actinic fluxes
- **Meteorological processes**
  - Wind field - Water vapor
  - Pressure - Density
  - Temperature -Turbulence
- **Surface processes**
  - Temp. and water content of
    - Soil, Water, Snow
    - Sea ice, Vegetation, Roads
    - Roofs
  - Surface energy/moisture fluxes
  - Ocean-atmosphere exchange
  - Ocean dynamics, chemistry

Meteorology and Air Pollution (Seinfeld and Pandis, 2016)

Meteorological Scales of Motions

1. *Microscale.* Phenomena occurring on scales of the order of 0–100 m, such as the meandering and dispersion of a chimney plume and the complicated flow regime in the wake of a large building.
2. *Mesoscale.* Phenomena occurring on scales of tens to hundreds of kilometers, such as land–sea breezes, mountain–valley winds, and migratory high- and low-pressure fronts.
3. *Synoptic Scale.* Motions of whole weather systems, on scales of hundreds to thousands of kilometers.
4. *Global Scale.* Phenomena occurring on scales exceeding 5×10^3 km.

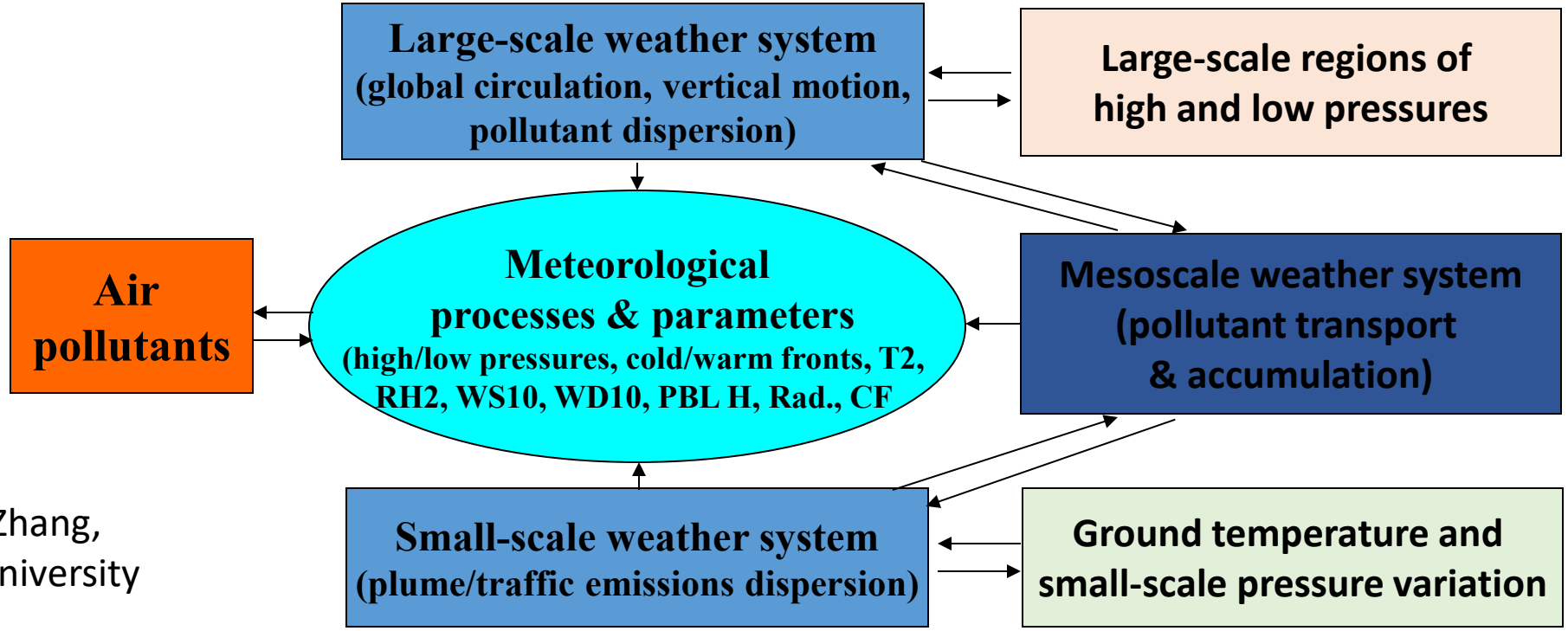
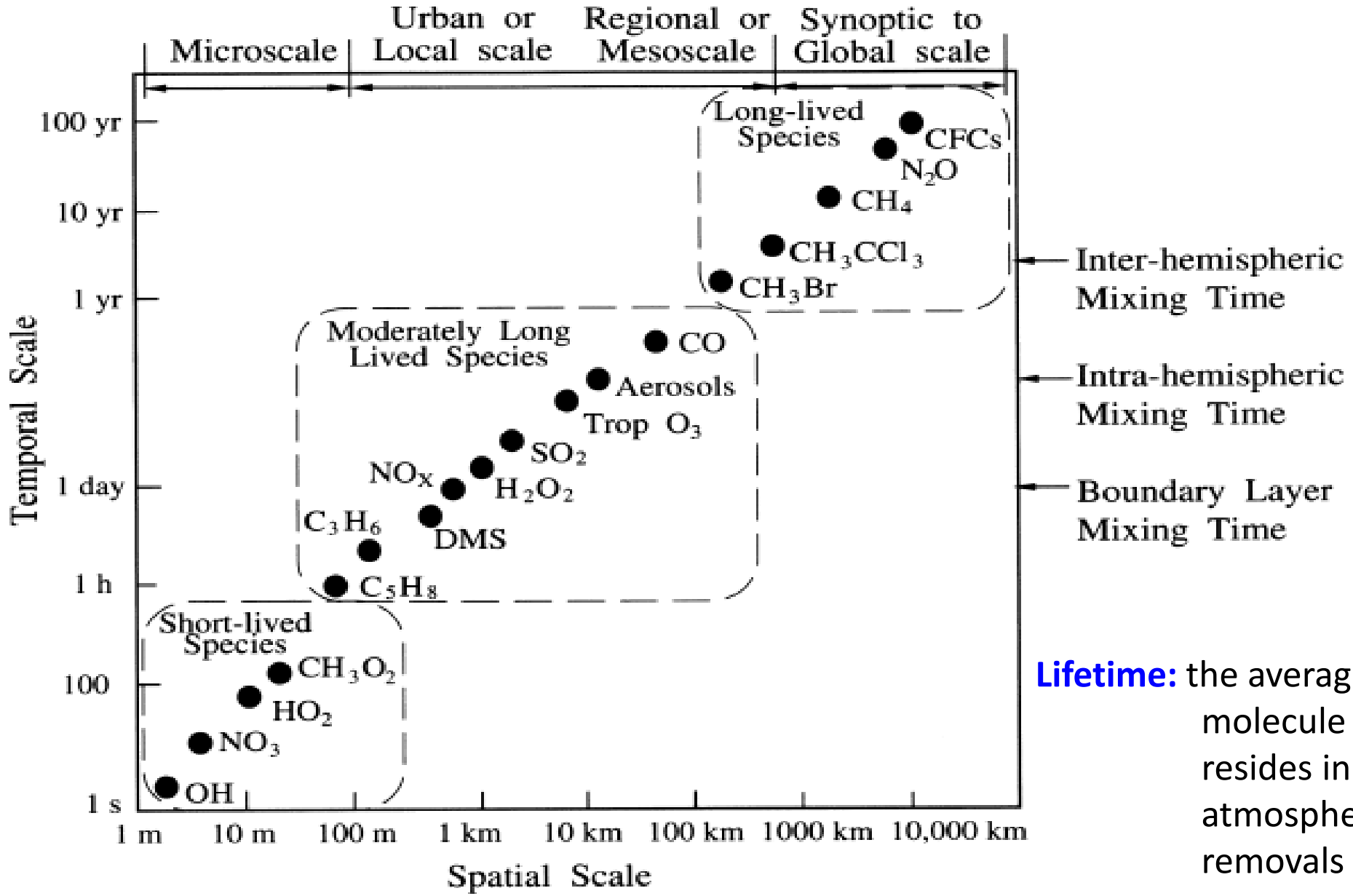


Figure by Yang Zhang, Northeastern University

Spatial and Temporal Scales of Atmospheric Processes

(Fig. 1.4, Seinfeld and Pandis, 2016)



Lifetime: the average time that a molecule of a species resides in the atmosphere before removals

Spatial Scales of Atmospheric Processes

(Seinfeld and Pandis, 2016)

TABLE 1.1 Spatial Scales of Atmospheric Chemical Phenomena

Phenomenon	Length scale, km
Urban air pollution	1–100
Regional air pollution	10–1000
Acid rain/deposition	100–2000
Toxic air pollutants	0.1–100
Stratospheric ozone depletion	1000–40,000
Greenhouse gas increases	1000–40,000
Aerosol–climate interactions	100–40,000
Tropospheric transport and oxidation processes	1–40,000
Stratospheric–tropospheric exchange	0.1–100
Stratospheric transport and oxidation processes	1–40,000

Effects of Large-Scale Pressure System on Air Pollution (Characteristics of Low and High Pressure Systems) (Table 6.2, Jacobson, 2012)

	Surface Low-Pressure Systems		Surface High-Pressure Systems	
Characteristic	Semiperm-anent	Thermal	Semiperm-anent	Thermal
Latitude range	45-65ºN	25-45ºN	25-45ºN	45-65ºN
Surface pressure gradients	Strong	Varying	Weak	Varying
Surface wind speeds	Fast	Varying	Slow	Varying
Surface wind directions	Converging, counter-clockwise	Converging, counter-clockwise	Diverging, clockwise	Diverging, clockwise
Vertical air motions	Upward	Upward	Downward	Downward
Cloud cover	Cloudy	Cloud-free or cloudy	Cloud free, sunny	Cloud free
Storm formation?	Yes	Sometimes	No	No
Effect on air pollution	Reduces	Reduces	Enhances	Enhances

Semipermanent pressure systems: formed over ocean. **surface high-pressure centers**-Subtropical high-P belts (Pacific high and Bermuda-Azores high in NH). **surface low-pressure centers**-subpolar low-P belts (Aleutian low and Icelandic low in NH)
Thermal pressure systems: formed over land by heating (low-P) or cooling (high-P) seasonally.

Effects of Large-Scale Meteorology (Jacobson, 2012)

Effect of Horizontal Transport

- Fast winds tend to clear out chemically produced pollution faster than do slow winds.
- Fast winds resuspend more soil dust and other particles from the ground than do slow winds.
- Wind direction determines where air pollutants are transported to/from.
- Long range transport enhances local-regional-hemispheric pollution buildup via transferring pollutants/precursors from sources regions downwind.

Effect of Vertical Transport

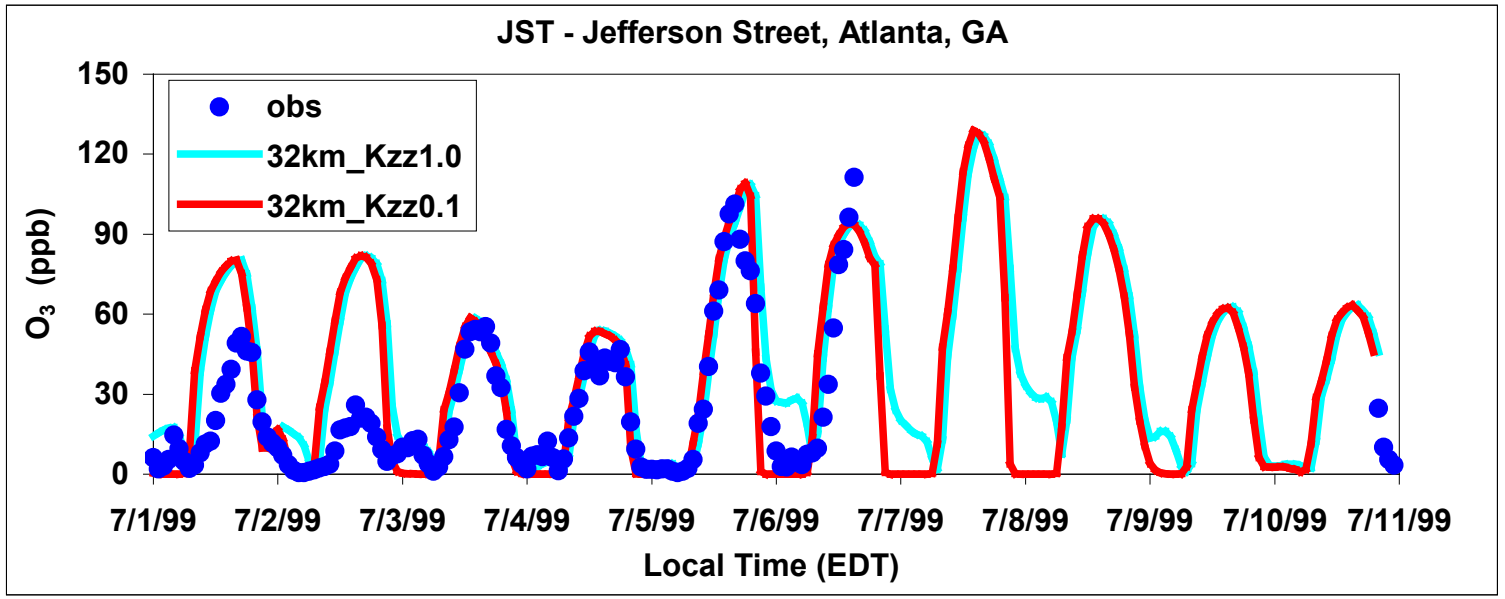
- Strong vertical mixing during daytime leads to low pollutant concentrations.
- Strong vertical mixing at night may lead to high concentrations for some pollutants (e.g., O_3).

Effect of Cloud Cover

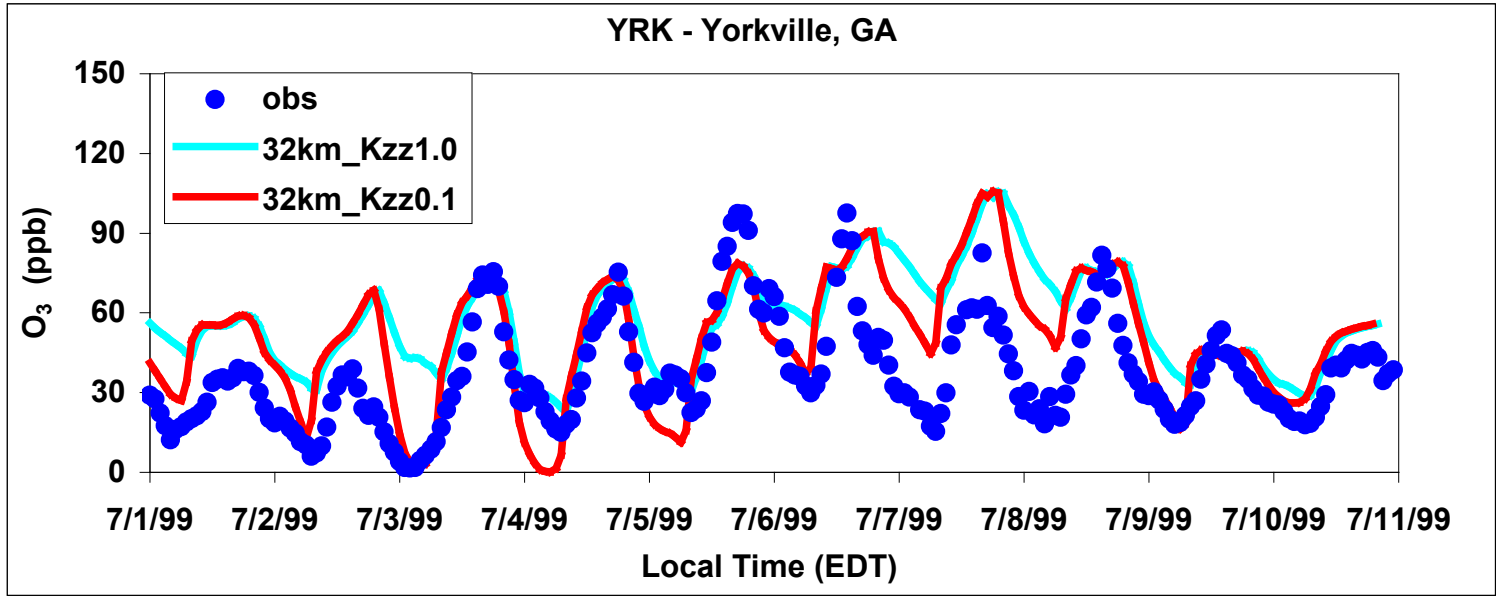
- Reduces the penetration of UV radiation, therefore decreasing rates of photolysis below them.
- Pollutants dissolve in cloud water and are either rained out or returned to the air upon cloud evaporation. Rain-forming clouds help to cleanse the atmosphere.
- Enhances aerosol formation via in-cloud chemistry.

Effect of Floor Values of Vertical Eddy Diffusivity Coefficient (K_{zz}) in CMAQ (Zhang et al., 2006)

Jefferson Street, Atlanta, Georgia, US



Yorkville, Georgia, US



Effects of Local-Scale Meteorology (Jacobson, 2012)

Effect of Ground Temperature

- Warm ground surfaces produce high inversion base heights (thick mixing depths) and low pollution mixing ratios. Cold ground surfaces produce thin mixing depths and high pollution mixing ratios.
- Warm surfaces enhance convection, causing surface air to mix with air aloft and resulting in faster near-surface winds and greater dispersion.
- Affect rates of several processes including rates of biogenic gas emissions from trees, chemical reactions, and gas-to-particle conversion.

Effect of Atmospheric Stabilities

- Affect plume dimension and dispersion and concentrations of pollutants downwind.

Effect of Soil Moisture

- Increases in soil liquid water can cool the ground, reduce convection and mixing depths, and slow near-surface winds. The net effect is to enhance pollutant buildup.

Effect of Urban Heat Island

- Urban construction material surfaces increase surface T, resulting in increased mixing depths, faster near-surface winds and lower near-surface concentrations of pollutants.

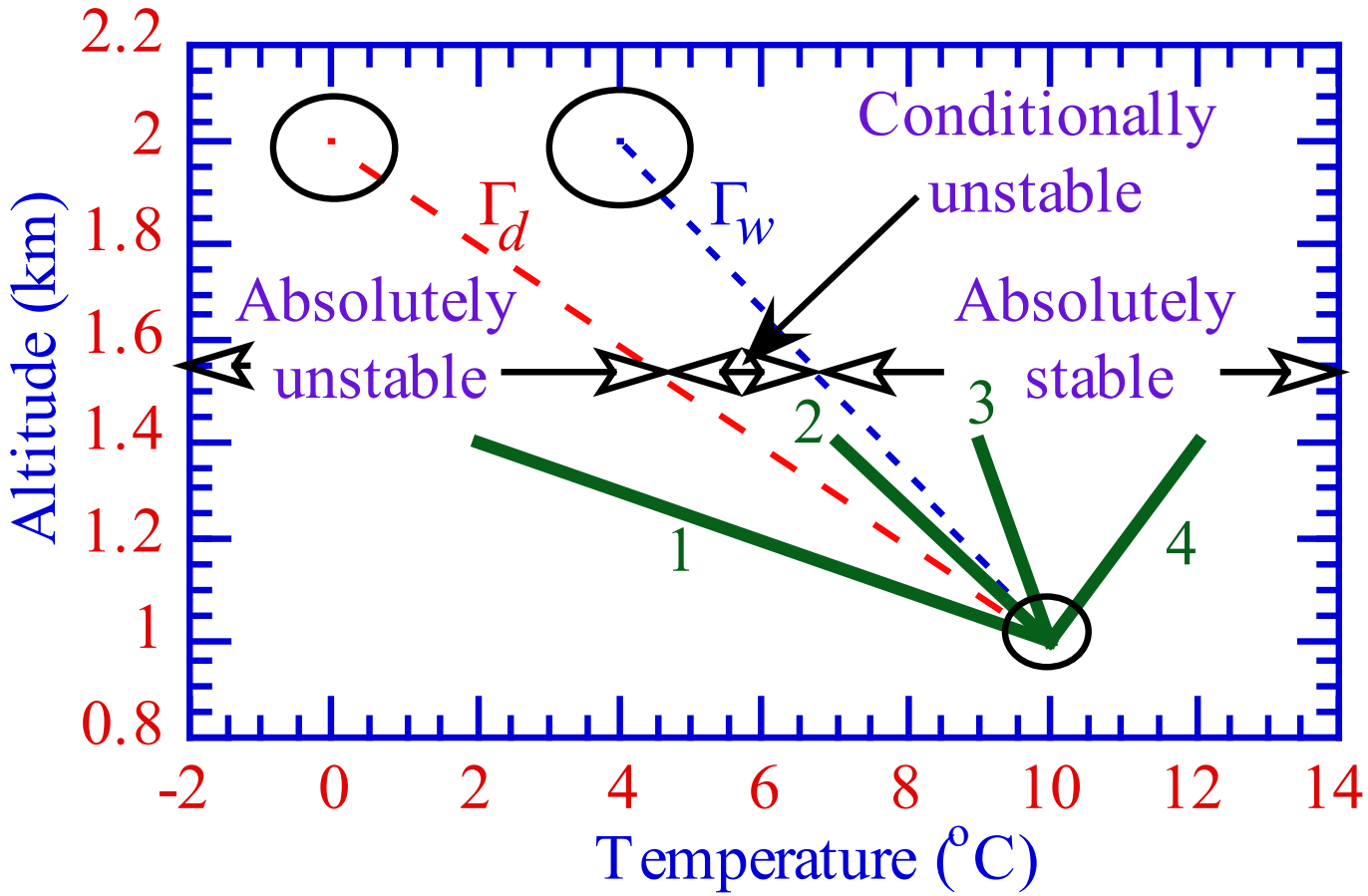
Effect of Sea/Valley Breezes

- Transfer primary pollutants emitted near the coast (e.g., LA) into inland (e.g., Riverside).
- Form elevated pollution layers by lifting and injecting polluted air into the inversion layer during its return flow to the ocean.

Atmospheric Stability (Fig. 6.9, Jacobson, 2012)

Stability – a measure of whether pollutants emitted will convectively rise and disperse or build up in conc. near the surface.

$\Gamma_e > \Gamma_d$	**Absolutely unstable (1)**
$\Gamma_e = \Gamma_d$	**Dry neutral**
$\Gamma_d > \Lambda > \Gamma_w$	**Conditionally unstable (2)**
$\Gamma_e = \Gamma_w$	**Wet neutral**
$\Gamma_e < \Gamma_w$	**Absolutely stable (3)**
$\Gamma_e < \Gamma_w, \Delta T/\Delta z > 0$	**Absolutely stable (inversion) (4)**



Γ_d – dry (or unsaturated) adiabatic lapse rate, = 9.8 K (or °C) km^{-1}

Γ_w – wet (or saturated, or pseudoadiabatic) lapse rate.

Γ_e – environmental lapse rate, $= -\Delta T/\Delta z$.

Temperature Inversion – air temperature increases with increasing height.

Type of Inversions (Jacobson, 2012)

Radiation (nocturnal) inversion – occurs nightly as land cools by emitting thermal IR radiation,leading to high conc. in the nocturnal PBL.

Large-scale subsidence inversion – occurs within a surface high-pressure system as air descends, compressing and warming adiabatically.

Marine inversion – occurs over coastal areas. As marine air moves inland during a sea breeze, it forces warm, inland air to rise, creating warm air over cold air.

Small-scale subsidence inversion – occurs when the air compresses and warms on top of cool air, as air flows down a mountain slope.

Frontal inversion – occurs in the low pressure system at the cold front where cold, dense air acts as a wedge and forces air in the warm air mass to rise, creating warm air over cold air.

Mixed layer – the unstable layer in direct contact with the surface
Mixing height (depth) – the height of mixed layer, a few hundreds meters to 3 km, typically 1 km.

Major Challenges of Air Pollution Meteorological Modeling (Seaman, 2020)

- **Use of remotely-sensed data for data assimilation**
- **Improved treatments for major physical processes in meteorology modeling**
  - Stable PBL and mix-layer characterization
  - Radiation
  - Moist and deep convection
  - Clouds (convective and shallow) and cloud processes
  - Land-surface exchanges
  - Turbulence
  - Aerosol-cloud interactions
- **Parameterizations needed for modeling at very fine grid spacing (< 100 m)**

Major Challenges in Air Pollution Meteorological Modeling

- **Use of mass-conserving finite-differencing for the prognostic equations in meteorological models to reduce mass-field errors introduced to air quality models**
  - Thunderstorms/precipitation
  - Thermal inversions
  - Low-level jet
- **Operational air quality forecasting – development of the coupled meteorology and chemistry models that allow feedbacks (e.g., the Weather Research and Forecast / Chemistry (WRF/Chem))**
- **Nowcasting support for homeland security**
  - Simulating the release of deadly airborne toxics
  - Predicting the transport of the toxic plume to guide an emergency response
- **Coupled air quality and regional climate modeling**

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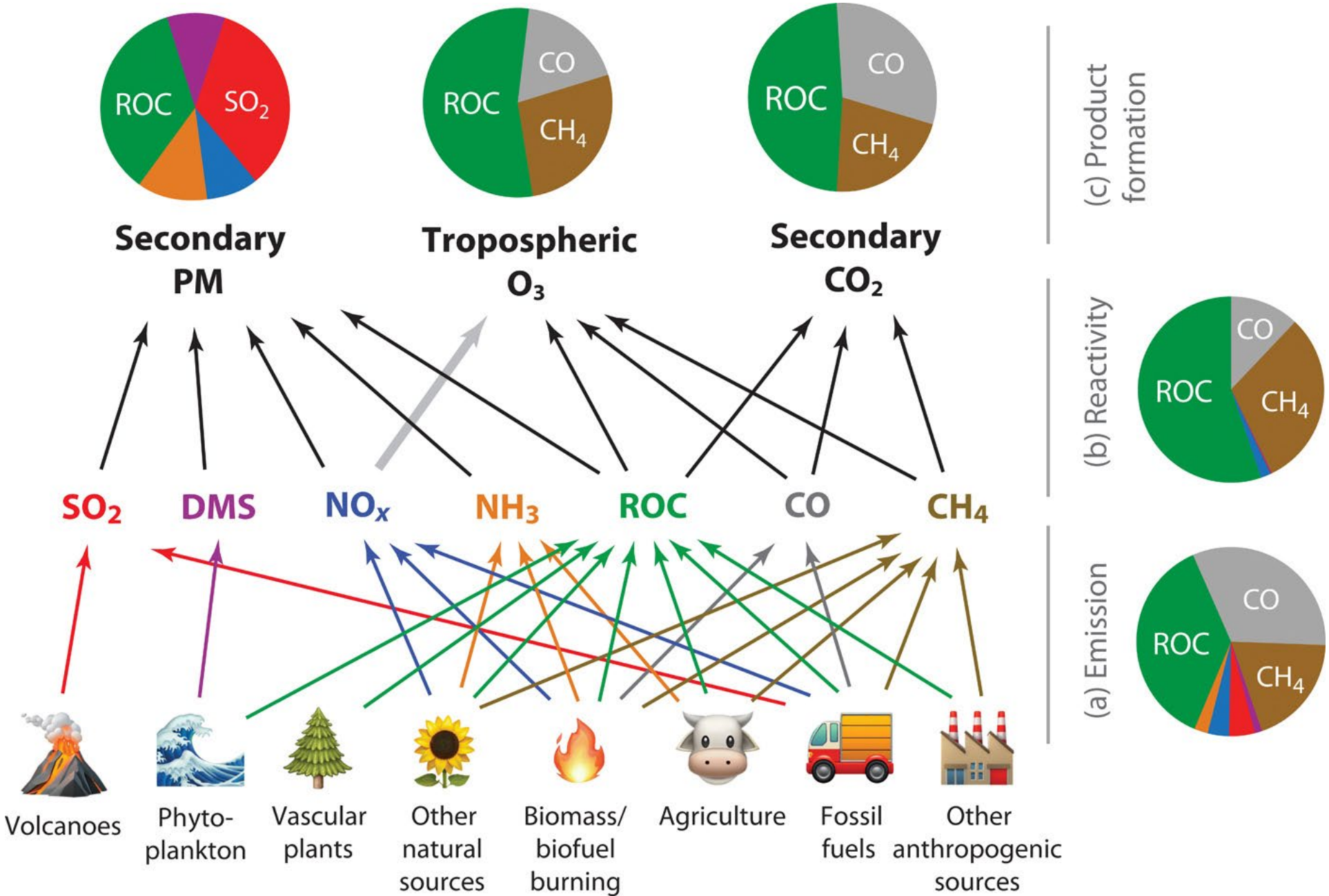
Importance of Atmospheric Chemistry

- Atmospheric chemistry affects the production, loss and concentrations of ozone (O_3), particulate matter (PM), atmospheric acids and other air pollutants. Important chemistry occurs in the gas-phase, aqueous-phase and heterogeneously (multiple phases are involved).
- Much of the gas-phase chemistry involves the oxidation of nitrogen oxides (NO_x = NO + NO_2) and volatile organic compounds (VOCs), which are most important precursors to O_3 in urban areas. Other O_3 precursors include CO and CH_4. Gas-phase chemistry plays a key role in determining the lifetime and distribution of O_3, hydrogen peroxide (H_2O_2) and other oxidants such as hydroxyl radical (HO) and the hydroperoxyl radical (HO_2)
- The gas-phase reactions that produce O_3, H_2O_2 and inorganic aerosols are linked to the chemistry that occurs in the aqueous and heterogeneous phases. HO reacts with NO_2 and SO_2 to produce nitric acid and sulfuric acid which both react with ammonia (NH_3) to produce ammonium nitrate, ammonium bisulfate and ammonium sulfate. Sulfuric acid, ammonium nitrate, ammonium bisulfate and ammonium sulfate are constituents of secondary inorganic aerosols. The gas-phase reactions of HO_x with VOCs may lead to the formation of secondary organic aerosol (SOA).
- Different gas-phase chemical mechanisms may lead to different predictions of gases, aerosols, and the resulting aerosol direct and indirect effects that will in turn affect the radiation, cloud and precipitation formation, as well as climate.

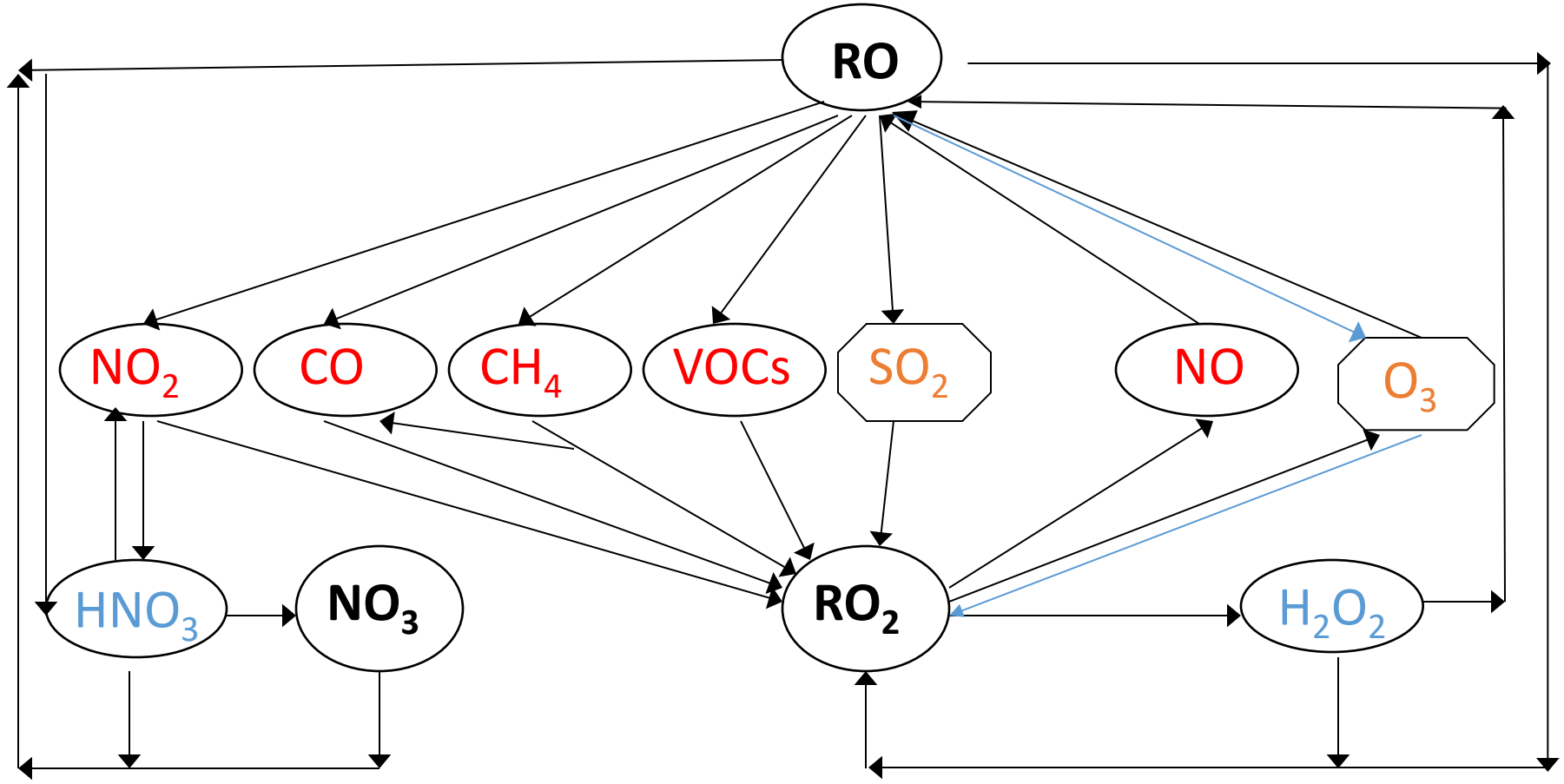
Air Pollutants for Different Problems (Table 3.4, Jacobson, 2012)

Indoor air pollution	Outdoor Urban air pollution	Acid precipitation	Stratospheric Ozone Reduction	Global Climate change
Gases				
Nitrogen diox.	Ozone	Sulfur dioxide	Ozone	Water vapor
Carbon monox.	Nitric oxide	Sulfuric acid	Nitric oxide	Carbon dioxide
Formaldehyde	Nitrogen dioxide	Nitrogen dioxide	Nitric acid	Methane
Sulfur dioxide	Carbon monox.	Nitric acid	Hydrochlor. acid	Nitrous oxide
Organic gases	Ethene	Hydrochlor. acid	Chlorine nitrate	Ozone
Radon	Toluene	Carbon dioxide	CFC-11	CFC-11
	Xylene		CFC-12	CFC-12
	PAN			
Aerosol-particle types or components				
Black carbon	Black carbon	Sulfate	Chloride	Black carbon
Organic matter	Organic matter	Nitrate	Sulfate	Organic matter
Sulfate	Sulfate	Chloride	Nitrate	Sulfate
Nitrate	Nitrate			Nitrate
Ammonium	Ammonium			Ammonium
Allergens	Soil dust			Soil dust
Asbestos	Sea spray			Sea spray
Fungal spores	Tire particles			
Pollens	Lead			
Tobacco smoke				

The sources of key reactive emissions into the atmosphere (Heald and Kroll, 2020)



Tropospheric Chemistry: Overview (Zhang, 2024)



R = H, CH_3, C_2H_5, etc.

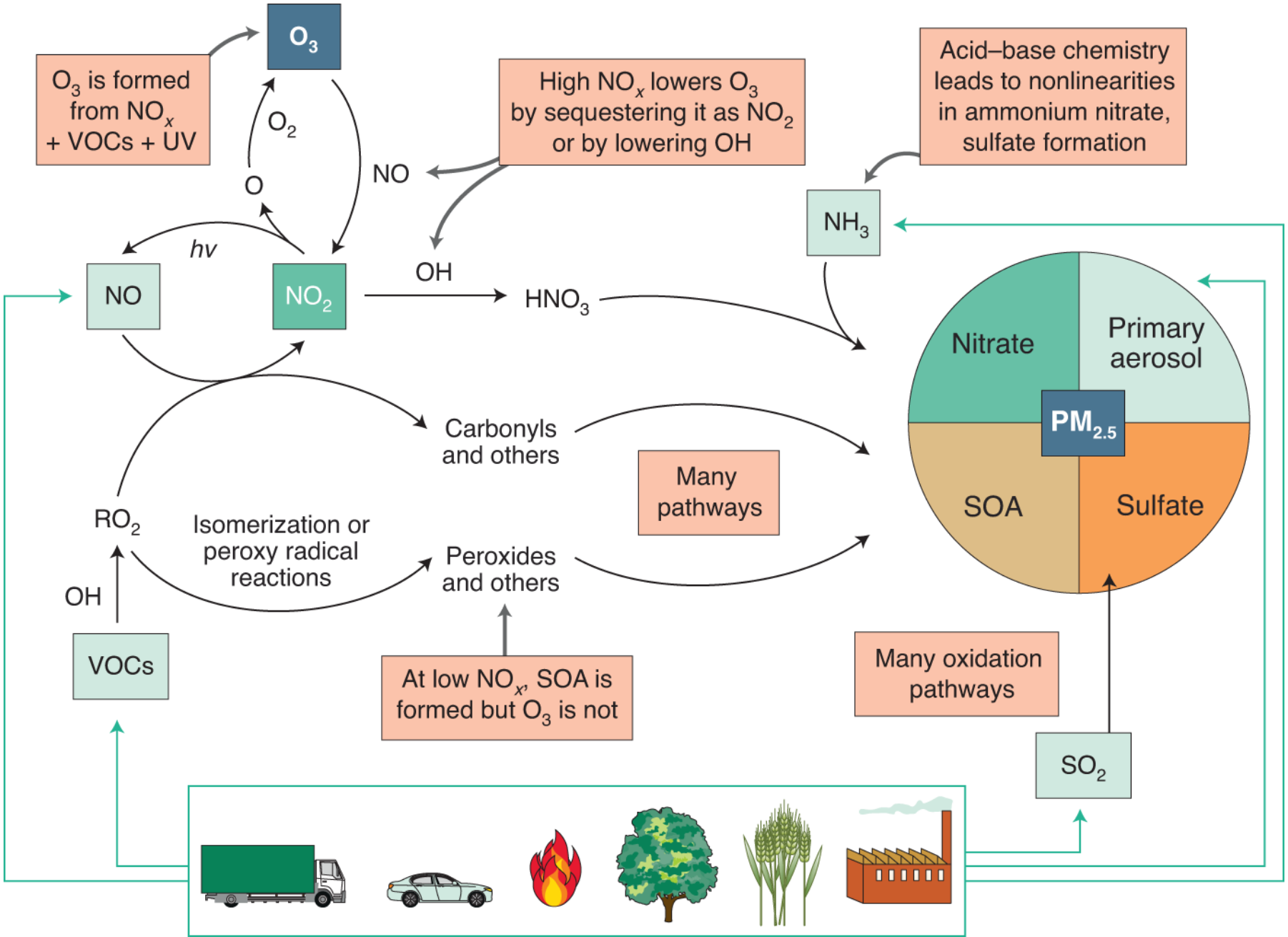
- Tropospheric chemistry is characterized by reaction cycles.
- Radicals (e.g., OH, HO_2, RO, RO_2, NO_3) play a key role.
- Reactions lead to removal as well as generation of pollutants.

RO-alkoxy radical

RO_2-alkyl peroxy radical

NO_3-nitrate radical

Simplified overview of the atmospheric chemistry of ozone and $PM_{2.5}$ formation (Kroll et al., 2020)

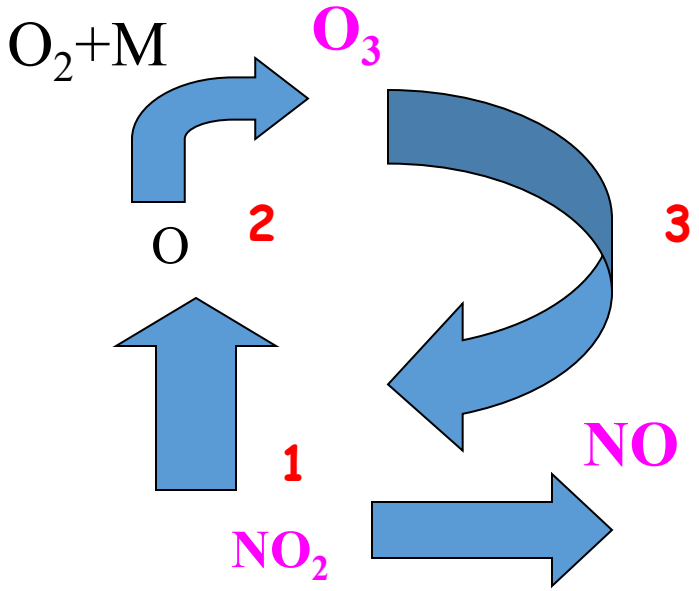


Basic Photochemical Cycle of NO_2, NO, and O_3 (Seinfeld and Pandis, 2016)

1. $NO_2 + h\nu \rightarrow NO + O$
2. $O + O_2 + M \rightarrow O_3 + M$

- **Net:** $NO_2 + O_2 \xrightarrow{h\nu} NO + O_3$

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



Photostationary-state relationship:

$$[O_3]_{ss} = \frac{j_1[NO_2]}{k_3[NO]}$$

Null cycle - *cycle* neither produces nor destroys anything overall

NO_x/CO Cycles in Free Troposphere (Seinfeld and Pandis, 2016)

In presence of NO_x

$$NO_2 \xrightarrow{h\nu} NO + O_3$$

In presence of CO, NO_x

$$NO_2 \xrightarrow{h\nu} NO + O_3$$

HO_2 regenerates NO_2 from NO.

$$NO_2 \xrightarrow{h\nu} NO + O_3 \quad \text{1, fast}$$

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

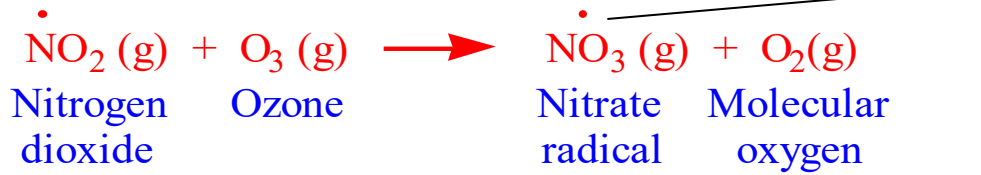
HO_2 regenerates OH from NO.

$$NO \quad \text{2, slow}$$

→ NO forms O_3 via its oxidation by HO_2 to NO_2, followed by the photolysis of NO_2

→ CO forms O_3 via increasing the ratio of NO_2 to NO

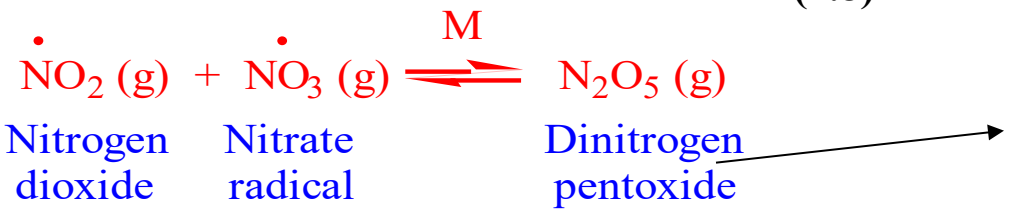
Nighttime Nitrogen Chemistry (Jacobson, 2012)



(4.8)

Present at night, because of the daily photolysis reaction that breaks it down:

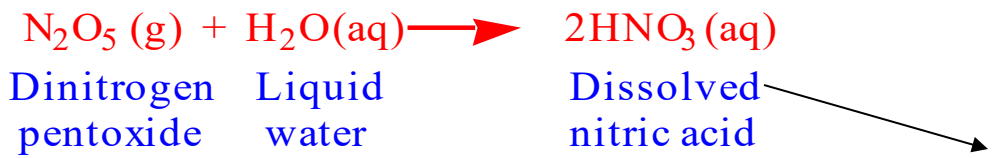
NO_3+hν → NO_2 + O λ < 0.41-0.67 μm
NO_3+hν → NO + O_2 λ < 0.59-0.63 μm



(4.9)

Present at night, because of photolysis and fast thermal decomposition at high temp:

N_2O_5+hν → NO_3 + NO_2 λ < 0.39 μm



(4.10)

Termination of the cycle: hydrolysis of N_2O_5 occurring on the aerosol/cloud droplet surfaces is much faster than that in the gas-phase.

Complete Nitrogen Chemistry (Warneck, 2000)

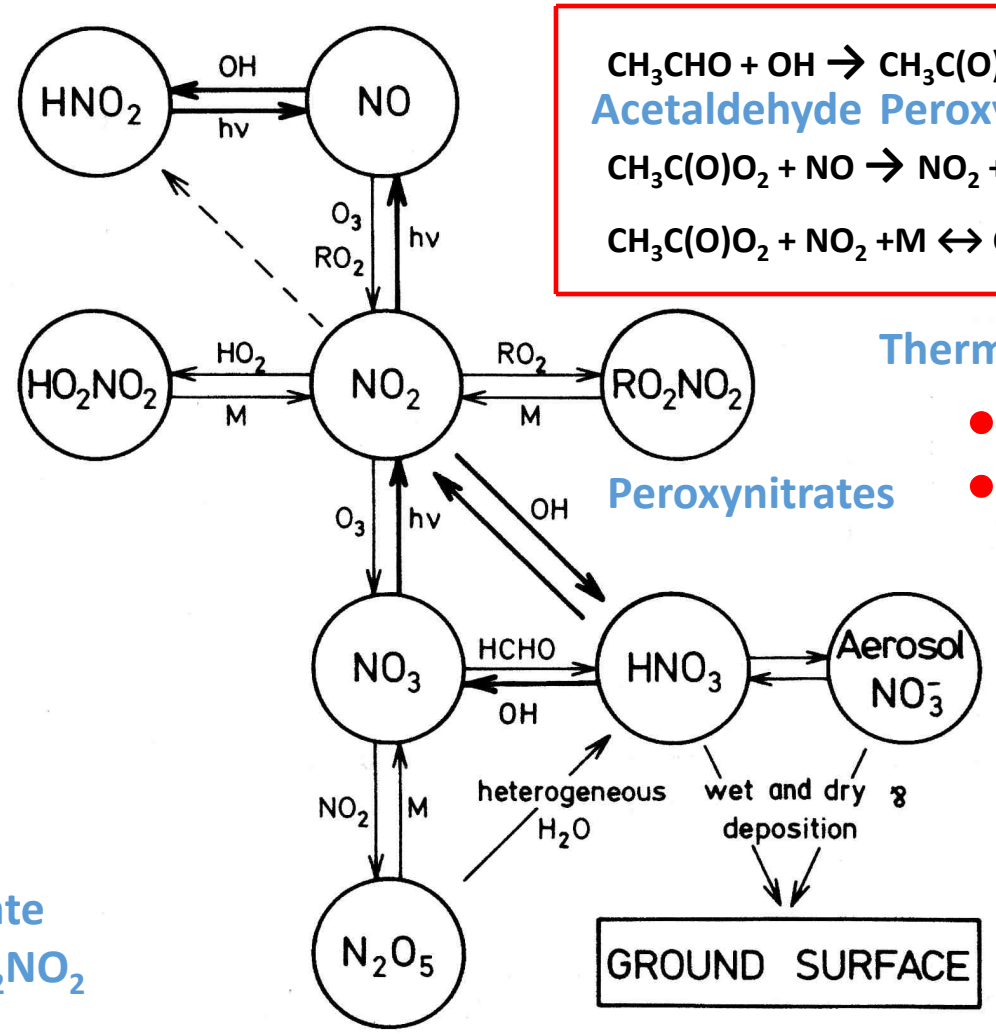
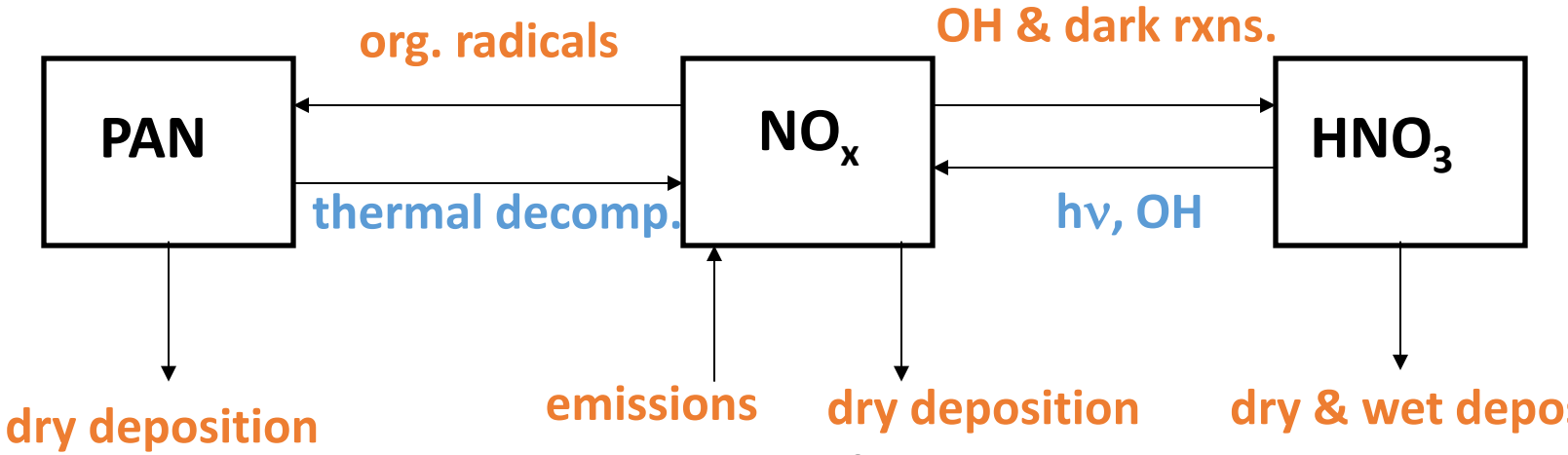


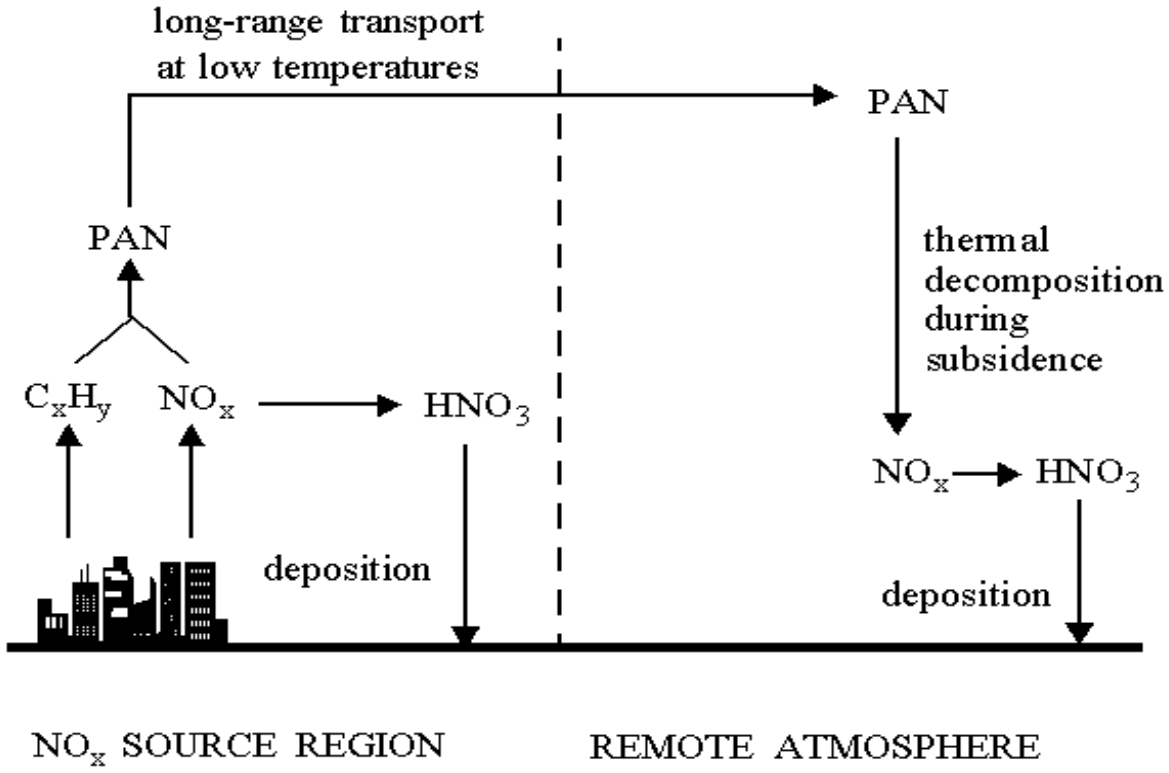
FIGURE 9.6 Oxidation scheme for nitrogen oxides and related compounds. Photochemical processes are indicated by bold arrows.

Simplified Schematic of Tropospheric NO_y Chemistry

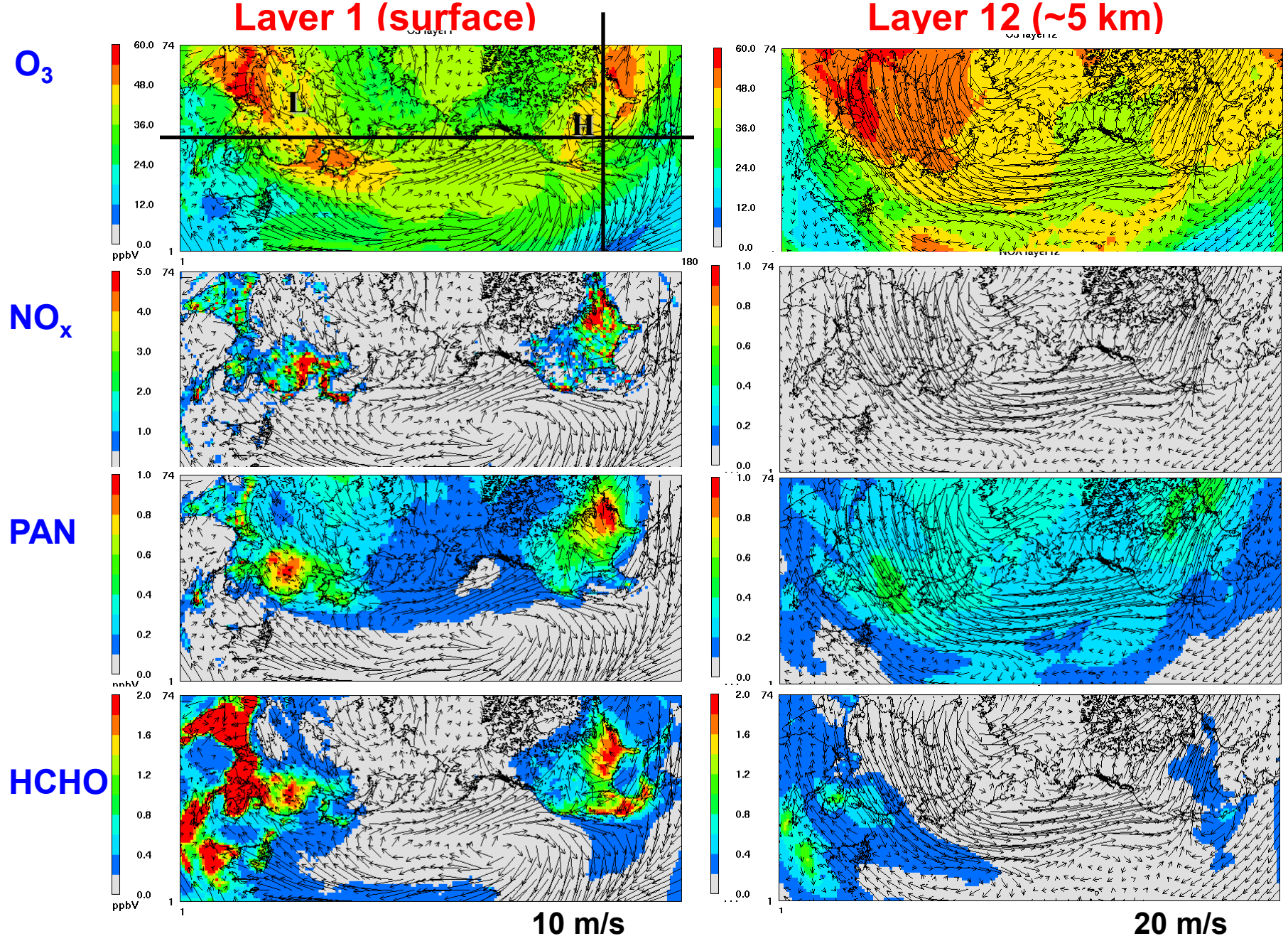
(Modified from Kasibhatla, 2003; Jacob, 2003; Zhang, 2024)



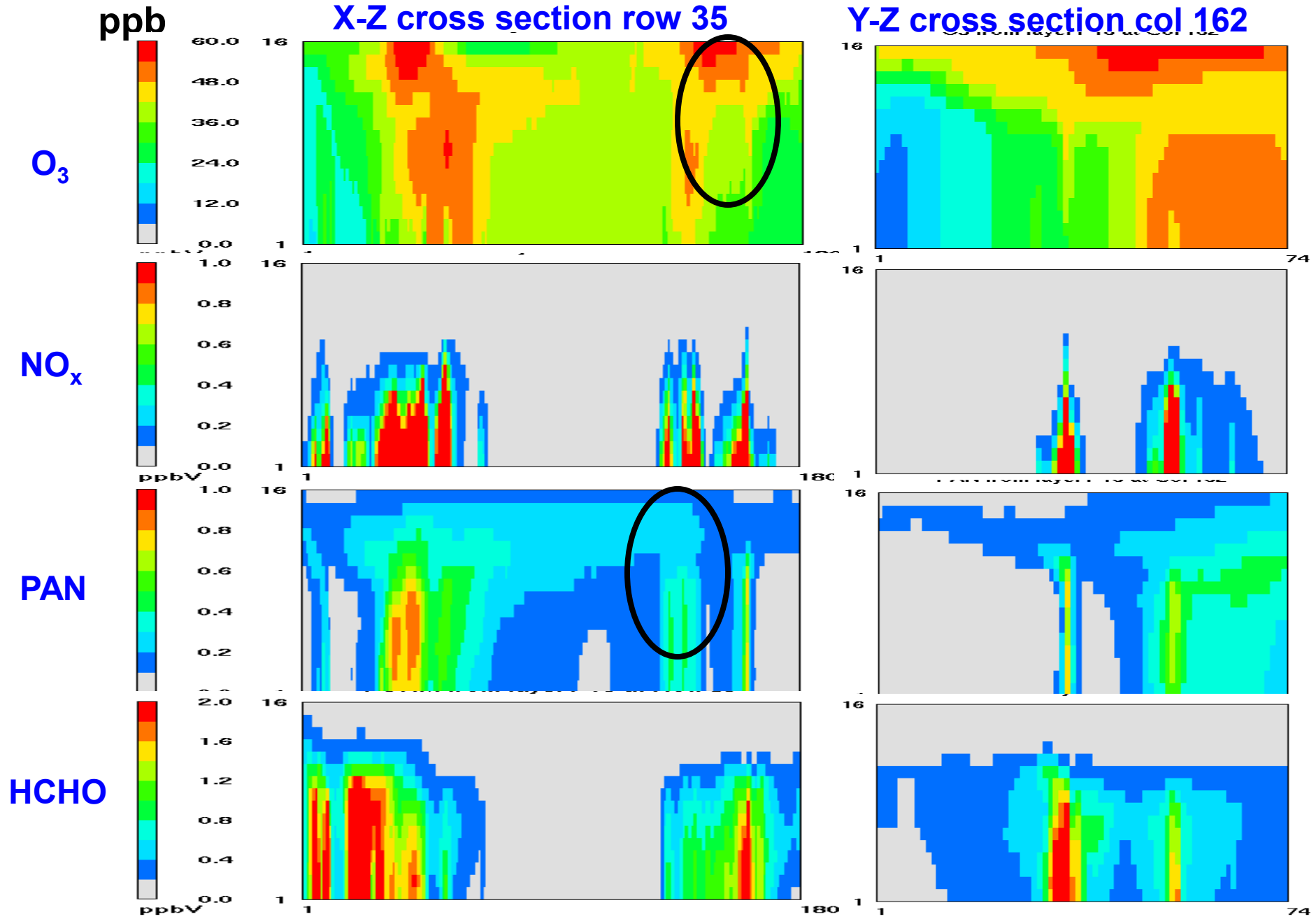
- PAN lifetimes: 30-min at 298 K, 8-hr at 273 K, and several months in upper troposphere
- Org. peroxynitrate reservoir (PAN, i.e., $CH_3C(O)O_2NO_2$) sequesters NO_x and facilitates long range-transport.
- Inorg. nitrate reservoir (HNO_3) facilitates the removal of NO_x



Spatial Distribution of Gaseous Species (Wang et al., 2012)



Vertical Distribution of Gaseous Species (Wang et al., 2012)

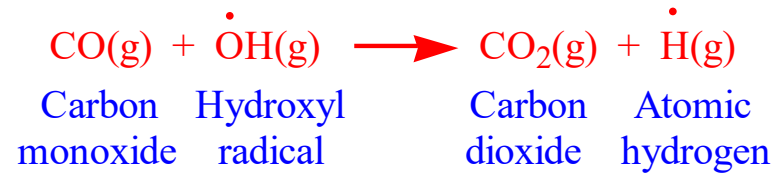


Role of NO_x in O_3 Chemical Production

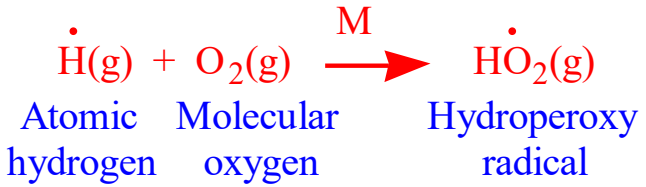
- Cycling of HO_x ($OH + HO_2$) and other peroxy radicals vs. radical termination reactions
- Too little NO_x: radical termination (e.g., $HO_2 + HO_2$) rather than radical cycling (e.g., $HO_2 + NO$) leading to O_3 chemical destruction (NO_x-limited O_3 chemistry)
- Too much NO_x: radical termination by alternate route (e.g., $OH + NO_2$) as well as short-term O_3 destruction by $NO + O_3 \rightarrow NO_2$ reaction → implications for O_3 peak downwind of strong NO_x sources (following titration of O_3 by NO in/near a plume)

Ozone Production From Carbon Monoxide (Jacobson, 2012)

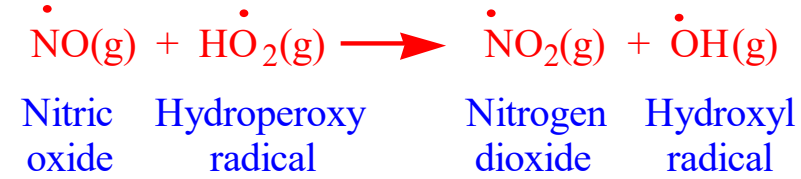
e-folding lifetime of CO due to R(4.11) is 28-110 days, R(4.11) does not interface with the photostationary-state relationship



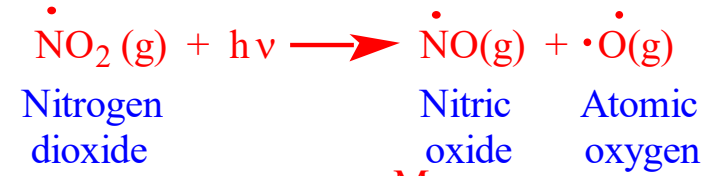
(4.11)



(4.12)

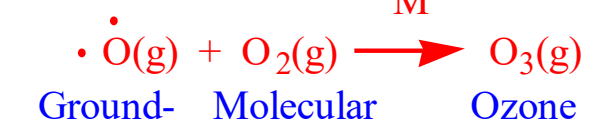


(4.13)



$\lambda < 420$ nm

(4.14)



(4.15)

→ **Form O_3 via increasing the ratio of NO_2 to NO**

Ozone Production From Methane (Jacobson, 2012)

e-folding lifetime of CH_4 due to R(4.16) is 8-12 years

$$CH_4(g) + \dot{O}H(g) \longrightarrow \dot{C}H_3(g) + H_2O(g)$$

Methane + Hydroxyl radical → Methyl radical + Water vapor

(4.16) **Abstraction**

$$\dot{C}H_3(g) + O_2(g) \xrightarrow{M} CH_3\dot{O}_2(g)$$

Methyl radical + Molecular oxygen → Methylperoxy radical

(4.17) **Addition**

$$\dot{N}O(g) + CH_3\dot{O}_2(g) \longrightarrow \dot{N}O_2(g) + CH_3\dot{O}(g)$$

Nitric oxide + Methylperoxy radical → Nitrogen dioxide + Methoxy radical

(4.18)

$$\dot{N}O_2(g) + h\nu \longrightarrow \dot{N}O(g) + \cdot\dot{O}(g) \qquad \lambda < 420 \text{ nm}$$

Nitrogen dioxide → Nitric oxide + Atomic oxygen

(4.19)

$$\cdot\dot{O}(g) + O_2(g) \xrightarrow{M} O_3(g)$$

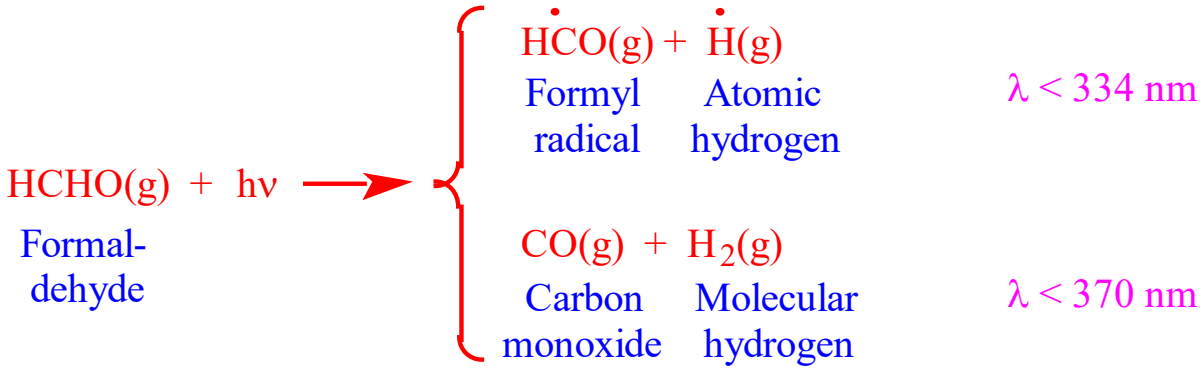
Ground-state atomic oxygen + Molecular oxygen → Ozone

(4.20)

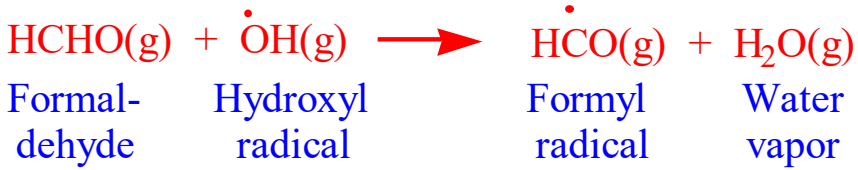
→ **Form O_3 via increasing the ratio of NO_2 to NO**

Abstraction- removes an atom from a compound (e.g., R(4.16))
Addition – a radical bounds to a compound (e.g., R(4.17))

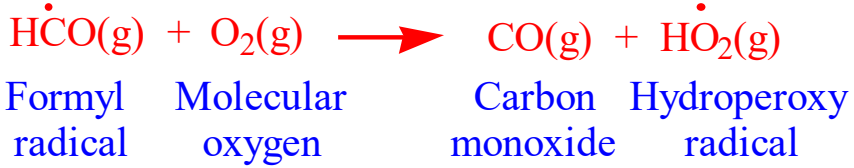
Ozone From Formaldehyde (Jacobson, 2012)



(4.22)



(4.23)



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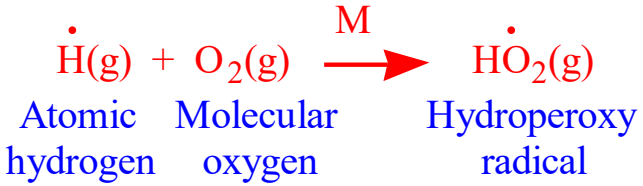


(4.25)

→ Form O_3 from both CO and HO_2

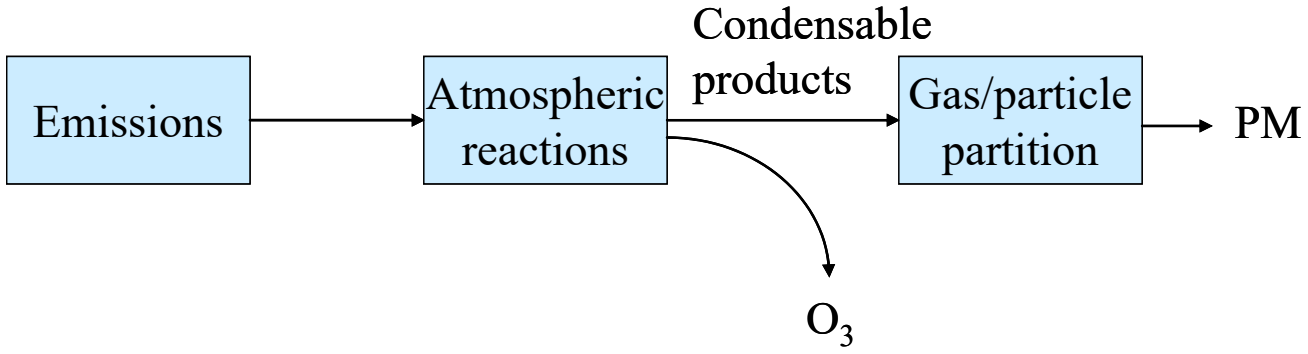
Lifetime of Reactive Organic Gases in Urban and Free Tropospheric Air (Jacobson, 2005, Table 11.5)

	Lifetime in Polluted Urban Air at Sea Level					
ROG Species	Photolysis	[OH] 5×10^6 molec. cm^{-3}	[HO_2] 2×10^9 molec. cm^{-3}	[O] 8×10^4 molec. cm^{-3}	[NO_3] 1×10^{10} molec. cm^{-3}	[O_3] 5×10^{12} molec. cm^{-3}
n-Butane	—	22 h	1000 y	18 y	29 d	650 y
trans-2-Butene	—	52 m	4 y	6.3 d	4 m	17 m
Acetylene	—	3.0 d	—	2.5 y	—	200 d
Toluene	—	9.0 h	—	6 y	33 d	200 d
Isoprene	—	34 m	—	4 d	5 m	4.6 h
Formaldehyde	7 h	6.0 h	1.8 h	2.5 y	2.0 d	3200 y
Acetone	23 d	9.6 d	—	—	—	—

	Lifetime in Free Tropospheric Air at Sea Level					
ROG Species	Photolysis	[OH] 5×10^5 molec. cm^{-3}	[HO_2] 3×10^8 molec. cm^{-3}	[O] 3×10^3 molec. cm^{-3}	[NO_3] 5×10^8 molec. cm^{-3}	[O_3] 1×10^{12} molec. cm^{-3}
n-Butane	—	9.2 d	6700 y	480 y	1.6 y	3250 y
trans-2-Butene	—	8.7 h	27 y	168 d	1.3 h	1.4 h
Acetylene	—	30 d	—	67 y	—	2.7 y
Toluene	—	3.8 d	—	160 y	1.8 y	2.7 y
Isoprene	—	5.7 h	—	106 d	1.7 h	23 d
Formaldehyde	7 h	2.5 d	11.7 h	67 y	40 d	16,000 y
Acetone	23 d	96 d	—	—	—	—

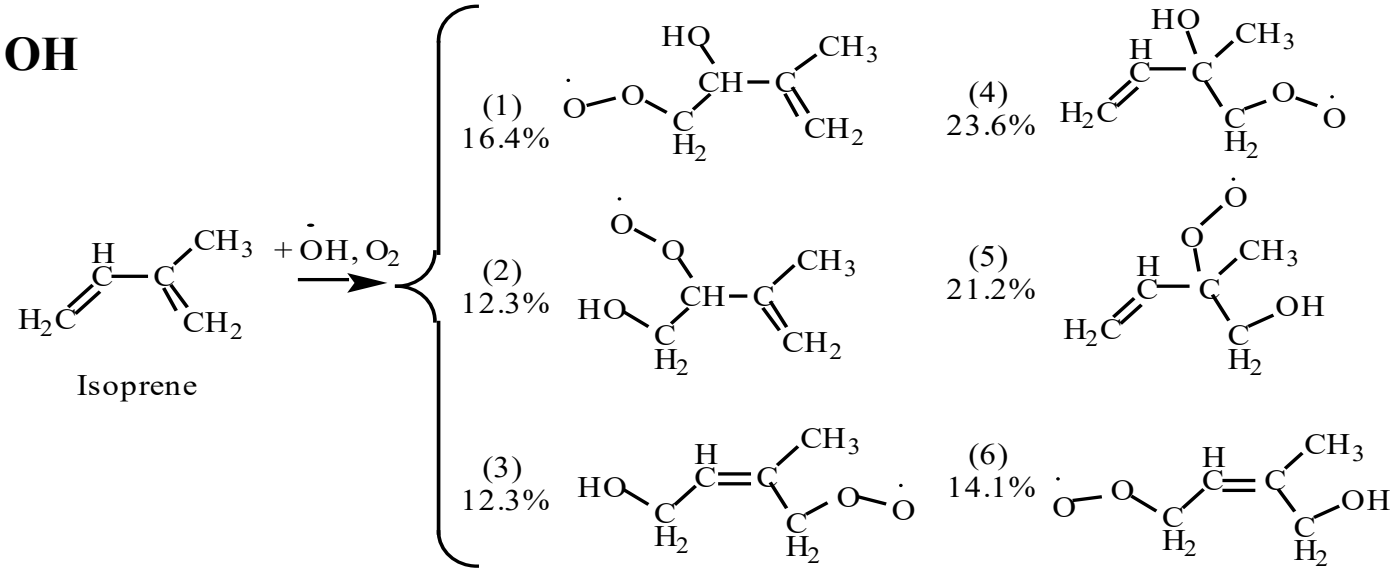
Atmospheric Biogenic VOCs

- **BVOCs are basically alkenes or cycloalkenes, and their chemistry is generally analogous to that of alkenes.**
- **Measurements of BVOCs can be made at a variety of scales, from leaf, branch, canopy, to landscape scales. These measurements provide information to develop and evaluate emission inventories.**
- **Of all the BVOCs, isoprene has been the most thoroughly studied. Its sources, emission rates, concentration ranges and chemical reactions are well known.**
- **BVOCs also highly reactive with OH, NO_3, and O_3 and are precursors to O_3 and PM formation.**



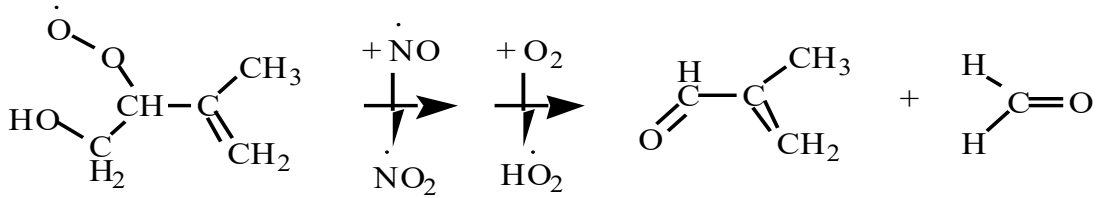
O_3 Production from Isoprene (Jacobson, 2012)

Isoprene oxidation by OH



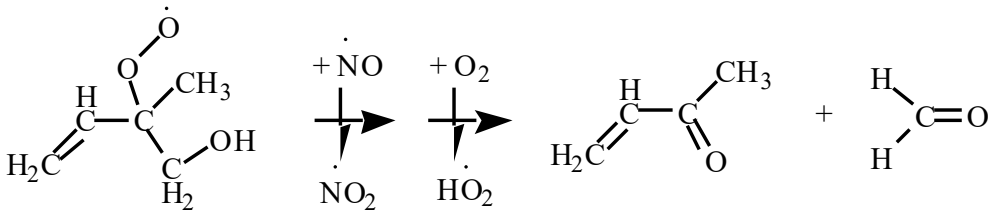
(4.54)

Methacrolein production via second product



(4.55)

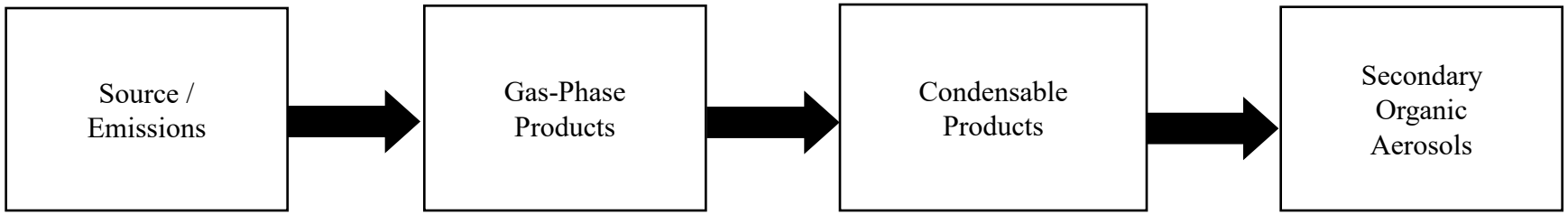
Methylvinylketone production via fifth product



(4.56)

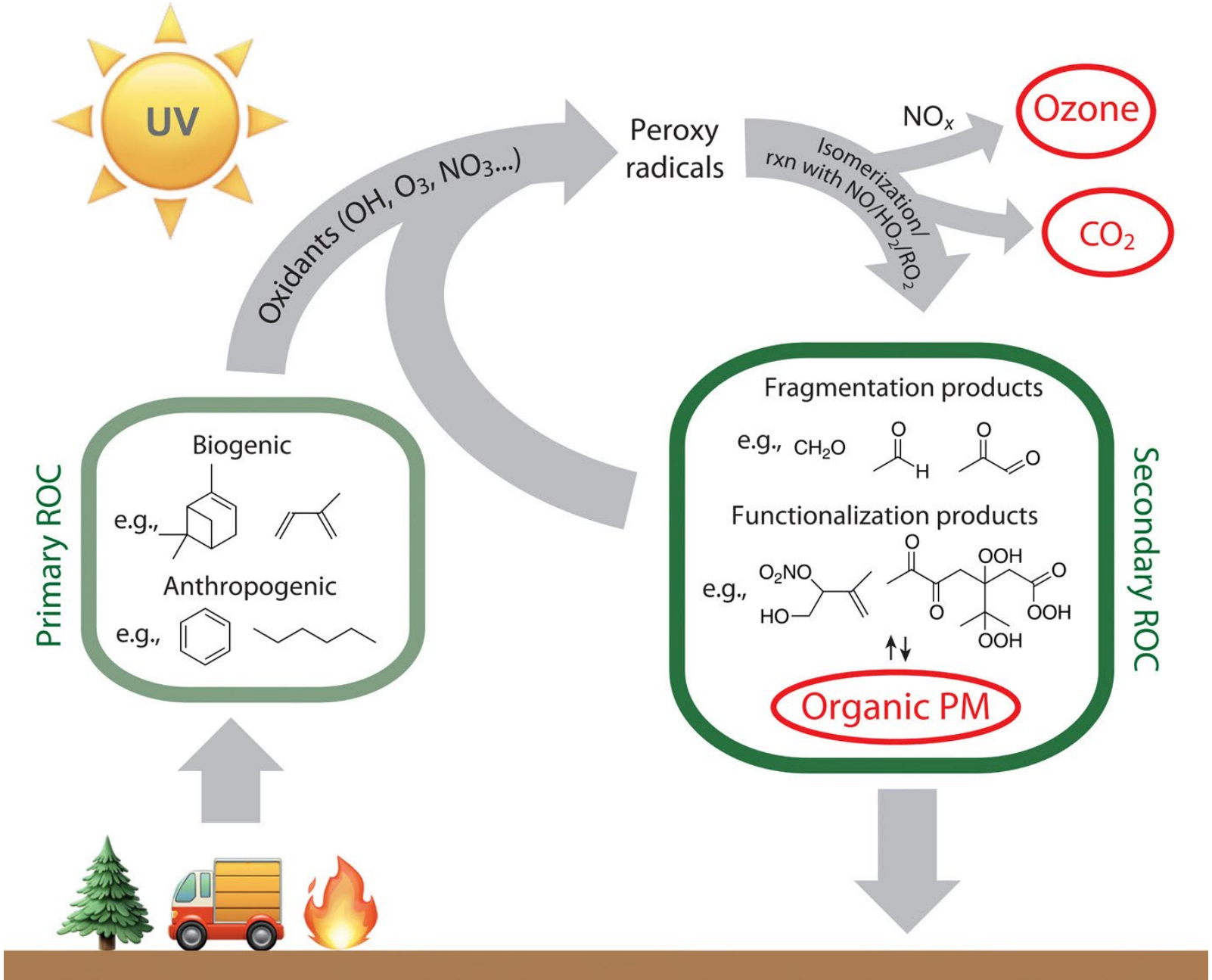
→Form O_3 via NO_2, HCHO

Formation of Secondary Organic Aerosols (Zhang, 2024)



- **Precursors**
  - **Anthropogenic: aromatics, olefins, paraffins, aldehydes**
  - **Biogenic: terpenes, sesquiterpenes, oxygenates, isoprene**
- **Oxidants: OH, NO_3, and O_3 (olefins only)**
- **Condensable products: acids, alcohols, carbonyls, ethers, β-caryophyllinic acid, 2-methyltetrols**
- **Processes leading to SOA formation**
  - **Absorption in an organic phase**
  - **Adsorption in an organic phase**
  - **Condensation onto existing particles**
  - **Dissolution in an aqueous phase**
  - **Heterogeneous reaction on surface of particles**
  - **Polymerization of second-generation products**
  - **Oligomerization (Accretion)**

Simplified atmospheric life cycle of ROC (Heald and Kroll, 2020)



Photochemical Smog Formation (Jacobson, 2012)

$$\underset{\text{Nitric oxide}}{\dot{N}O(g)} + \underset{\text{Organic peroxy radical}}{R\dot{O}_2(g)} \longrightarrow \underset{\text{Nitrogen dioxide}}{\dot{N}O_2(g)} + \underset{\text{Organic oxy radical}}{R\dot{O}(g)} \qquad (4.37)$$

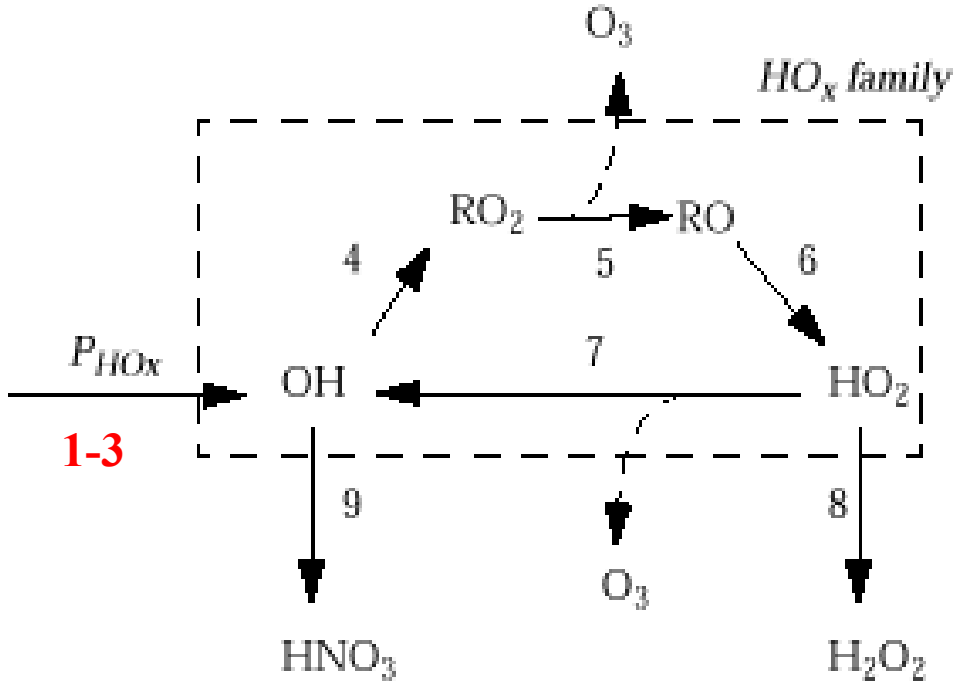
$$\underset{\text{Nitric oxide}}{\dot{N}O(g)} + \underset{\text{Ozone}}{O_3(g)} \longrightarrow \underset{\text{Nitrogen dioxide}}{\dot{N}O_2(g)} + \underset{\text{Molecular oxygen}}{O_2(g)} \qquad (4.38)$$

$$\underset{\text{Nitrogen dioxide}}{\dot{N}O_2(g)} + h\nu \longrightarrow \underset{\text{Nitric oxide}}{\dot{N}O(g)} + \underset{\text{Atomic oxygen}}{\cdot\dot{O}(g)} \qquad \lambda < 420 \text{ nm} \qquad (4.39)$$

$$\underset{\text{Ground-state atomic oxygen}}{\cdot\dot{O}(g)} + \underset{\text{Molecular oxygen}}{O_2(g)} \xrightarrow{M} \underset{\text{Ozone}}{O_3(g)} \qquad (4.40)$$

Schematic of O_3 Pollution Chemistry (Jacob, 1999)

1. $O_3 + hv \rightarrow O_2 + O(^1D)$
2. $O(^1D) + M \rightarrow O + M$
3. $H_2O + O(^1D) \rightarrow 2OH$
4. $RH + OH \rightarrow RO_2 + H_2O$
5. $RO_2 + NO \xrightarrow{O_2} RO + NO_2$
6. $RO + O_2 \rightarrow R`CHO + HO_2$
7. $HO_2 + NO \rightarrow OH + NO_2$
8. $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$
9. $OH + NO_2 + M \rightarrow HNO_3 + M$



(dominant under low NO_x conditions)

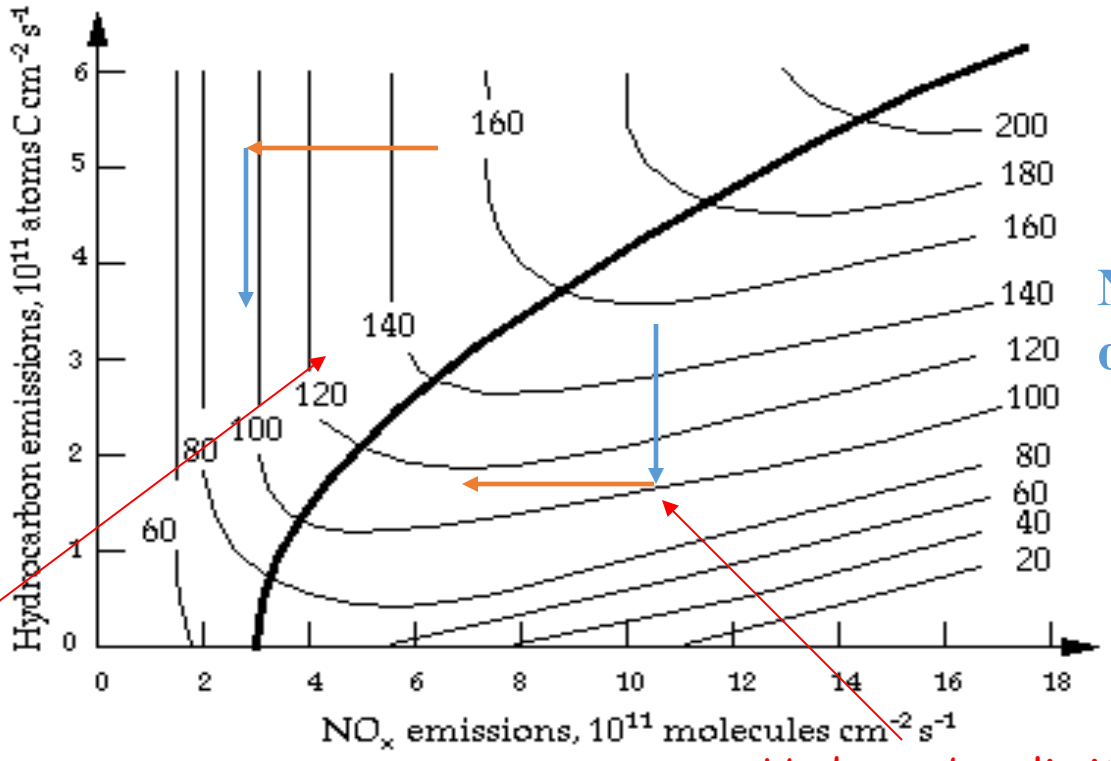
(dominant under very high NO_x conditions)

Net rxns 1-7:
$RH + 4O_2 \rightarrow R'CHO + 2O_3 + H_2O$

Ozone Isopleth: NO_x- and VOC-Limited Regimes

Empirical Kinetic Modeling Approach (EKMA Diagram)

(Jacob, 1999; Jacobson, 2005)



Ridge line

Nonlinearity of O_3 Chemistry

NO_x limited

$P_{O_3} = 2k_7(P_{HO_x}/2k_8)^{1/2}[NO]$

NOx-limited: decrease VOCs, no effect on O_3

Hydrocarbon limited

$P_{O_3} = (2k_4P_{HO_x}[RH])/(k_9[NO_2][M])$

VOC-limited: decrease NO_x, O_3 increases

Observed Mixing Ratios of Atmospheric Sulfur Gases and Their Lifetimes

(Seinfeld and Pandis, 2016)

TABLE 2.3 Average Lifetimes and Observed Mixing Ratios of Tropospheric Sulfur Compounds

		Mixing Ratio, ppt			
Species	Average Lifetime	Marine air	Clean Continental	Polluted Continental	Free Troposphere
H_2S	2 days	0–110	15–340	0–800	1–13
OCS	7 years	530	510	520	510
CS_2	1 week	30–45	15–45	80–300	≤ 5
CH_3SCH_3	0.5 day	5–400	7–100	2–400	≤ 2
SO_2	2 days	10–200	70–200	100–10,000	30–260
SO_4^{2-}	5 days	5–300[a]	10–120	100–10,000	5–70

[a]Nonseasalt sulfate.

Source: Lelieveld et al. (1997).

Reaction of Sulfur Oxides (Seinfeld and Pandis, 2006)

1. $SO_2 + OH + M \rightarrow HSO_3 + M$

Sulfur dioxide — Bisulfite

lifetime of SO_2 against reactions 1-3 is ~1 wk

2. $HSO_3 + O_2 \rightarrow HO_2 + SO_3$

Bisulfite — Hydroperoxy radical — Sulfur trioxide

3. $SO_3 + H_2O + M \rightarrow H_2SO_4 + M$

Sulfuric acid

- Net: $SO_2 + OH + O_2 + H_2O \rightarrow H_2SO_4 + HO_2$

Removal by dry and wet deposition

Sulfate Formation Mechanisms (Jacobson, 2012; Zhang et al., 1994)

Gas-Phase Oxidation (3-step)

(1) Gas-phase oxidation of SO_2 (g) to H_2SO_4(g);
(2) Condensation of H_2SO_4 (g) and H_2O(g) onto aerosol particles or cloud drops to produce an H_2SO_4(aq)-H_2O(aq) solution;
(3) The dissociation of H_2SO_4 (aq) to SO_4^{2-} in the solution.

Aqueous-Phase Oxidation (3-step)

(1) Dissolution of SO_2 (g) into liquid-water drops to produce SO_2(aq);
(2) In-drop conversion of SO_2 (aq) to H_2SO_3(aq) and dissociation of H_2SO_3(aq) to HSO_3^- and SO_3^{2-};
(3) In-drop oxidation of HSO_3^- and SO_3^{2-} to SO_4^{2-} in the solution.

Heterogeneous Chemistry (2-step)

(1) Uptake of SO_2 on the surface of preexisting aerosol
(2) Oxidized via heterogeneous reactions to form SO_4^{2-} on the surface of aerosols

Condensed Mechanisms for Organic Chemistry used in 3-D Air Quality Models (Zhang, 2024)

Carbon Bond Lumping (or lumped structure method) – individual organic gases are segregated into one or more bond groups that have similar chemical reactivity (e.g., CB- IV, CB05)

Carbon Bond Mechanism IV (CB-IV) and 2005 CB Mechanism (CB05)

- PAR (paraffins) -- single-bonded carbon atoms
- OLE (olefins) -- double-bonded carbon atoms
- ALD2 – acetaldehyde and higher aldehydes
- TOL (Toluene)-- 7-carbon aromatics
- XYL (Xylene) -- 8-carbon aromatics

Lumped species method – species of similar chemical reactivity are lumped together (e.g., RADM2 or Statewide Air Pollution Research Center gas-phase mechanism (SAPRC99, SAPRC07))

The Regional Acid Deposition Mechanism Version 2 (RADM2)

- HC3 – Alkanes with $2.7 \times 10^{-13} < k_{OH} < 3.4 \times 10^{-12}$
- HC5 -- Alkanes with $3.4 \times 10^{-12} < k_{OH} < 6.8 \times 10^{-12}$
- HC8 -- Alkanes with $6.8 \times 10^{-12} < k_{OH}$

Lumped surrogate species method – all species of similar chemical reactivity are grouped together (e.g., CACM)

The Caltech Atmospheric Chemistry Mechanism (CACM)

- ALKL – Lumped alkanes with C2-C6 (2-methyl-butane)
- OLEL – Lumped alkenes C3-C6 (1-pentene)

Differences: properties are based on an average for all species in that group in the lumped species method and based on that for a particular species in the lumped surrogate species

Gas-phase chemical mechanisms used in 3-D air quality models (Zhang and Baklanov, 2019)

(The symbol + indicates that the information was not apparent from the mechanism description)

N	Mechanism	Number of Chemical Species	Number of Chemical Reactions	Number of Photochemical Reactions	Number of Heterogeneous Reactions	Aqueous Chemistry	Model(s)	Reference
3	CBM-IV/CB4	33	70	11	NA	NA	NMMB/BSC-CTM, BOLCHEM, RACMO2/LOTOS-EUROS, WRF-Chem	Gery et al. (1989)
4	CBM-05/CB05	52	133	23	NA	NA	NMMB/BSC-CTM, WRF-CMAQ, C-IFS, CAMx	Sarwar et al. (2008)
5	CBM-Z	55-56	156	+	NA	NA	RegCM-Chem, Enviro-HIRLAM, WRF-Chem	Zaveri and Peters (1999)
6	CB06	77	190	28	NA	NA	CAMx	Yarwood et al. (2010)
8	GEOS-CHEM	80	>300	+	N_2O_5 & NO_3 $\rightarrow$ HNO_3 in sulfate	NA	RegCM-Chem	Bey et al. (2001)
14	MOZART2	63	132	32	N_2O_5 & NO_3 on sulfate	NA	ECHAM5/6-HAMMOZ	Horowitz et al. (2003)
15	MOZART3	108	218	18	71	NA	IFS-MOZART	Kinnison et al. (2007)
19	RADM2	63	136	21	NA	NA	MCCM, M-SYS, REMO,WRF-Chem, M-SYS	Stockwell et al. (1990)
20	RACM	77	214	23	NA	NA	COSMO-LM-MUSCAT, MCCM, Meso-NH, RegCM-Chem,MEMO/MARS, WRF- Chem	Stockwell et al. (1997)
21	RACM2	119	321	42	NA	NA	CMAQ, WRF-Chem, POLAIR3D	Goliff et al. (2013)
28	SAPRC99	72	182	35	NA	NA	RAMS/ICLAMS, CMAQ, CAMx, WRF-Chem	Carter (2000)
29	SAPRC07	44-207	126-640	+	NA	NA	CMAQ, CHIMERE	Carter (2010)
30	SAPRC99	72	182	35	NA	NA	RAMS/ICLAMS, CMAQ, CAMx, WRF-Chem	Carter (2000)

Major Issues In O_3 and $PM_{2.5}$ Pollution Control (Zhang, 2015, 2024)

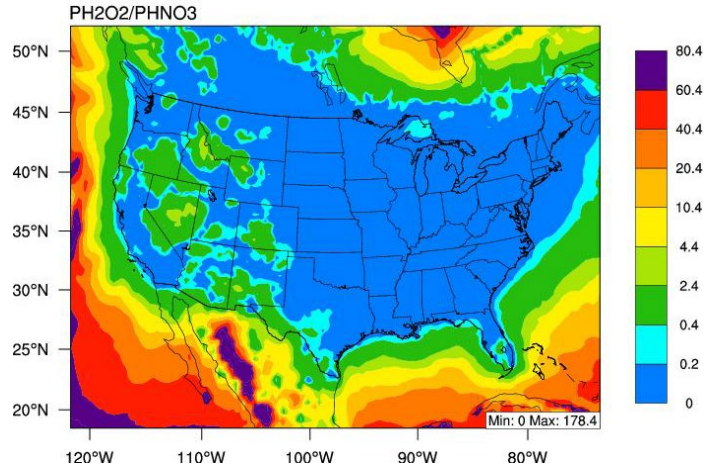
- **Questions:**
  - To what degree should NO_x and VOCs emissions be reduced to control O_3 and $PM_{2.5}$ pollution? Does $PM_{2.5}$ pollution control require controlling of emissions of additional precursors (SO_2, NH_3)?
  - How can we improve controls on dispersed primary emissions of $PM_{2.5}$ (which are a large source of exposure to billions of people in developing countries)?
  - How much O_3 and $PM_{2.5}$ can be formed from biogenic VOCs?
  - What source category contributes the most to the O_3 and PM pollution
  - What role does regional/intercontinental transport play in urban/local pollution control?
  - Are emission control strategies effective for both O_3 and $PM_{2.5}$?
  - Do emission control strategies of certain species co-benefit air quality control and climate change mitigation?

- **Uncertainties**
  - Reliability of emission inventories (e.g., natural hydrocarbon inventories)
  - Reliability of air quality models (e.g., local vs transported NO_x/VOCs/O_3)
  - Robustness of source apportionment methods
  - Poor characterization of VOC species and their chemical kinetics
  - Role of heterogeneous and aqueous-phase reactions

Case 1. O_3 Chemical Regimes over U.S. in 2001 (CMAQ/PA)

(Zhang et al., 2009)

Jan.



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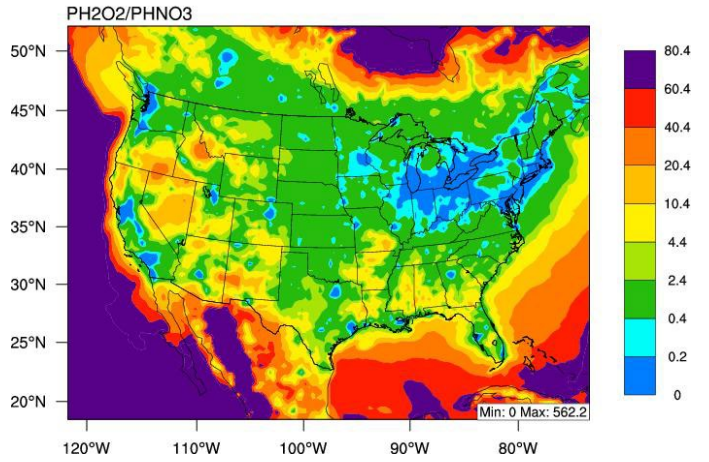

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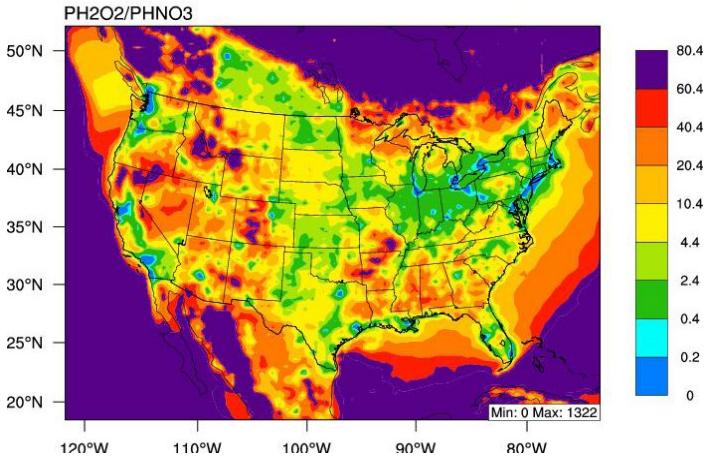

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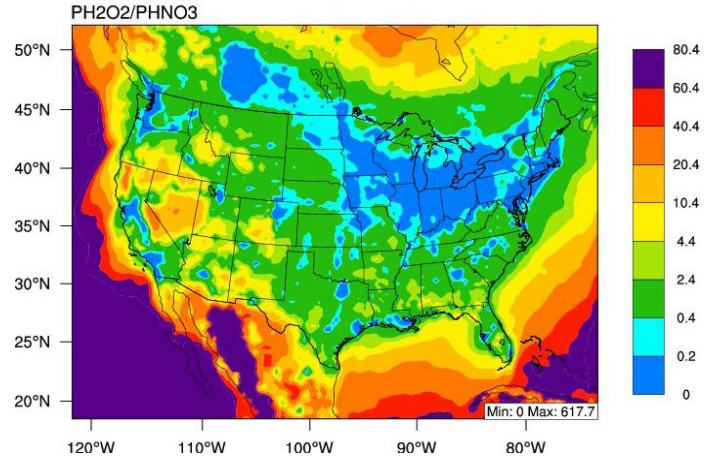
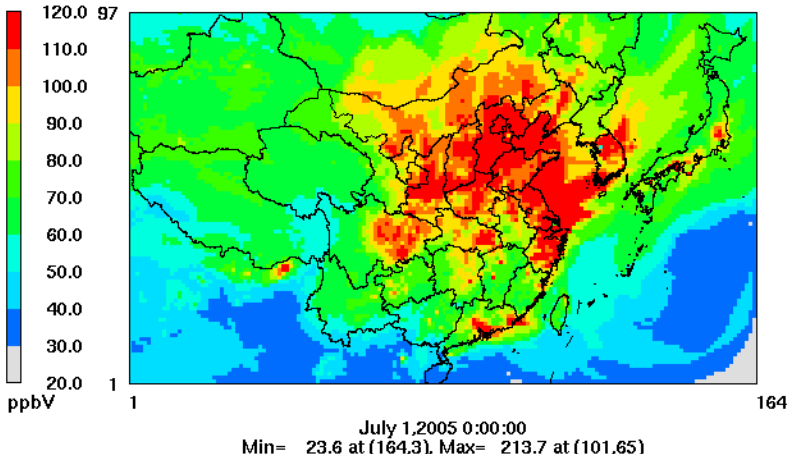


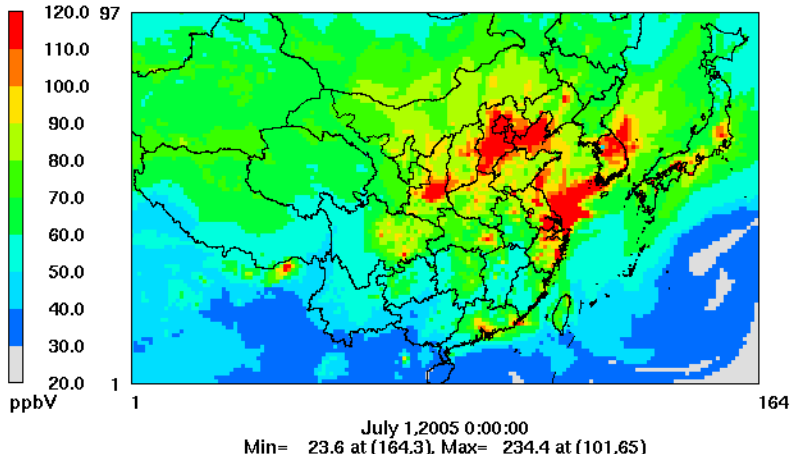
$PH_2O_2/PHNO_3$: NO_x-limited (≥ 0.2), and VOC-limited (< 0.2)

Case 2. CMAQ Simulation of 2005 Over China: NO_x Control Benefit for O_3 (July max.) (Jang et al., 2007)

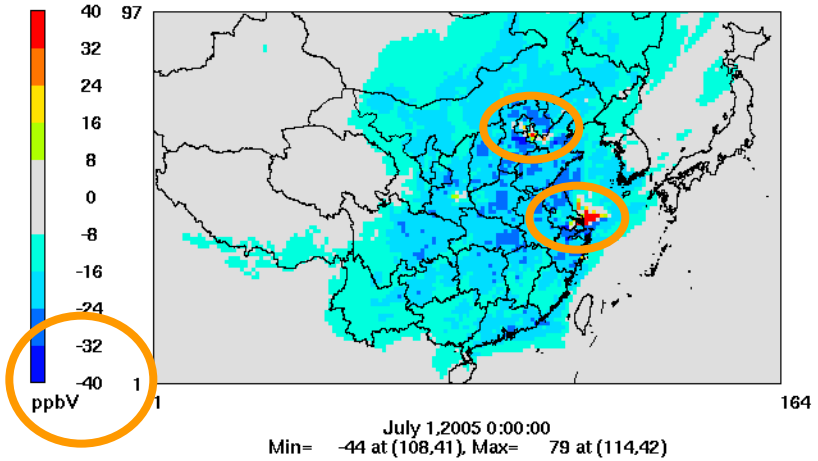
2010 Growth (59%)



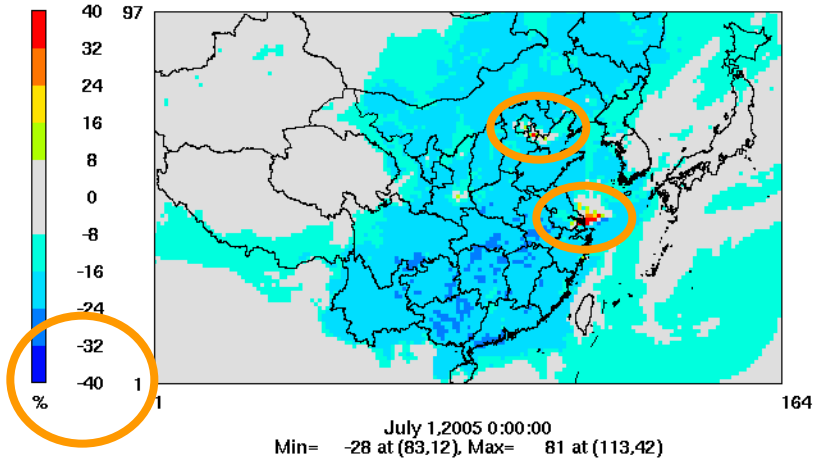
2010 NO_x Control (-10%)



Δ Diff.: (Control – Growth)



Δ %: (Control – Growth)



Case 3. Responses of $PM_{2.5}$ and O_3 in LA to Emission Reductions (Meng et al., 1997; Pai et al., 2000)

	50% VOC		50% NO_x	
	SAQM-AERO	CIT	SAQM-AERO	CIT
O_3	- 31%	- 34%	- 10%	- 6%
$PM_{2.5}$	+ 1%	+ 19%	- 24%	- 18%

CIT (Meng et al., Science, 277, 116-119, 1997)
SAQM-AERO (Pai et al., JAWMA, 50, 32-42, 2000)

Summary

- Atmospheric processes are very complex yet important in affecting the sources, transport, and impacts of air pollutants on human health and climate. Meteorological and other processes affect the transport and evolution of all air pollutants. Atmospheric chemistry plays a key role in formation of secondary air pollutants.
- Secondary air pollutants such as O_3 and PM are produced through a sequence of gas-phase, aqueous-phase, and heterogeneous chemical reactions. Key atmospheric radicals are OH, HO_2, and RO_2 that oxidize NO_x and VOCs to form O_3 and PM including secondary organic aerosol. Accurate emissions of gaseous precursors of O_3 and PM as well as primary PM emissions are critical for air quality modeling forecasting.
- The gas-phase, aqueous-phase, and heterogeneous mechanisms used in air quality models range from highly detailed to very condensed. The aggregation scheme for VOCs and the level of detail are the major differences between the gas-phase chemical mechanisms.
- Air quality modeling and forecasting and the development of synergetic O_3 and $PM_{2.5}$ pollution control strategies require understanding of fundamentals of atmospheric chemistry and processes

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