Atmospheric Chemistry and Aerosol

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Outline

- Importance of Atmospheric Chemistry and Aerosol
- Tropospheric Gas-Phase Chemistry
  - Chemistry of NOx, CO, VOCs, and O_3
  - Gas-phase chemical mechanisms used in CW-AQF models
- Atmospheric Aerosol
  - Classification and sources
  - Size distribution and chemical composition
  - Thermodynamics and dynamic processes
  - Formation mechanisms of secondary inorganic and organic aerosol
- Major Issues In O_3 and $PM_{2.5}$ Pollution Control
- Summary

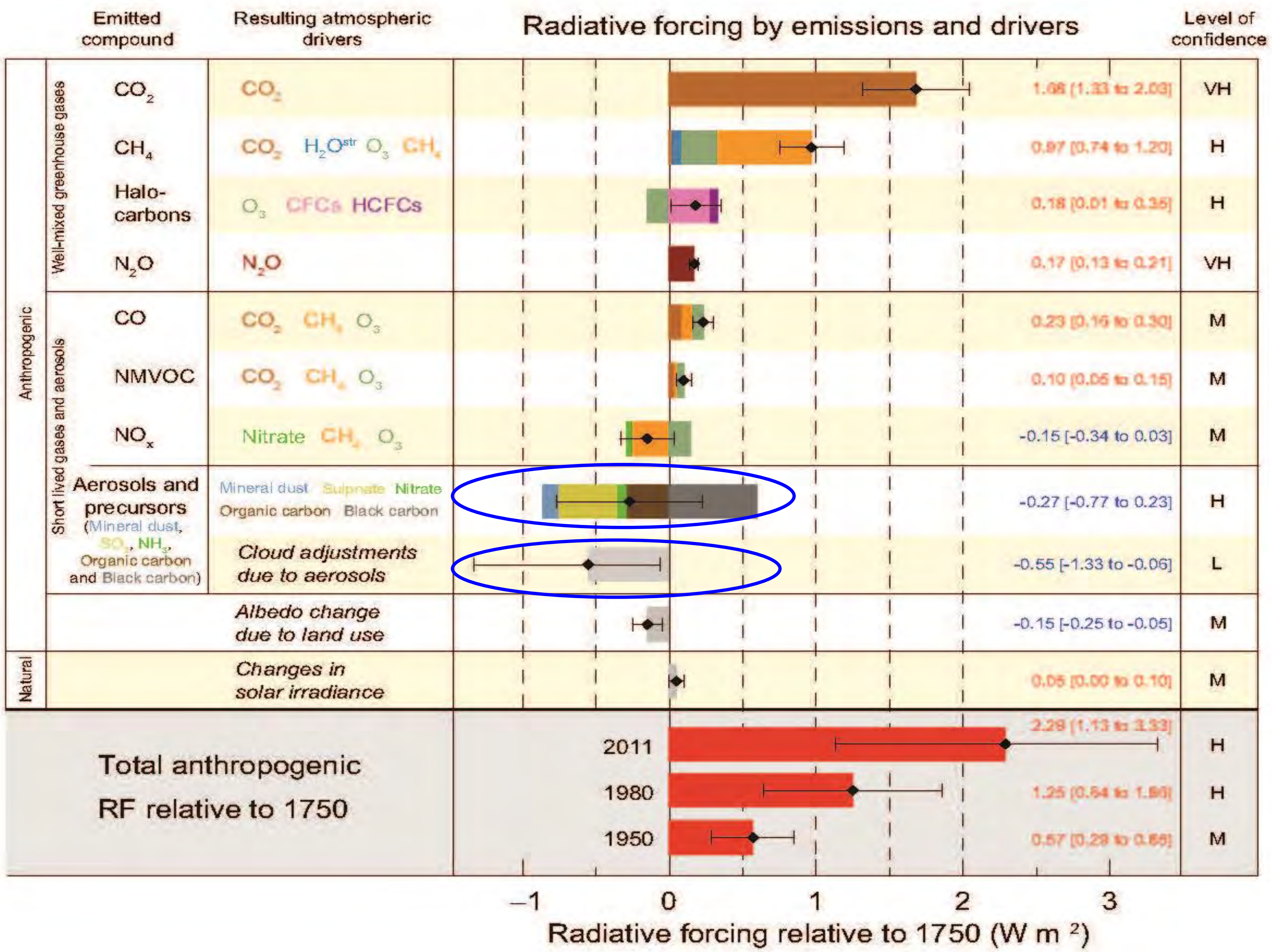
Sources: Zhang et al. (2012a, b), Zhang and Baklanov (2019), and Zhang (2015) and (2020)

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 O3 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.

Drivers of Anthropogenic Climate Change

IPCC - Intergovernmental Panel on Climate Change, AR5, **2013**)



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Tropospheric Chemistry on Earth: Overview

- **Due to abundance of O_2, earth's atmosphere is oxidizing (e.g., $SO_2 \rightarrow H_2SO_4$; $CH_4 \rightarrow CO$; $NO_2 \rightarrow HNO_3$)**
- **After O_2, O_3 is the most abundant oxidant. But direct oxidation of non-radical species by reaction with O_2 and O_3 is too slow to be of consequence**
- **The OH radical is the most important oxidant in the troposphere. O_3 is the primary source of tropospheric OH (Photolysis of O_3, followed by the reaction of a small fraction of the resulting $O(^1D)$ atoms with water vapor)**
- **Earth's atmospheric chemistry is characterized by reaction cycles involving radicals. 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**

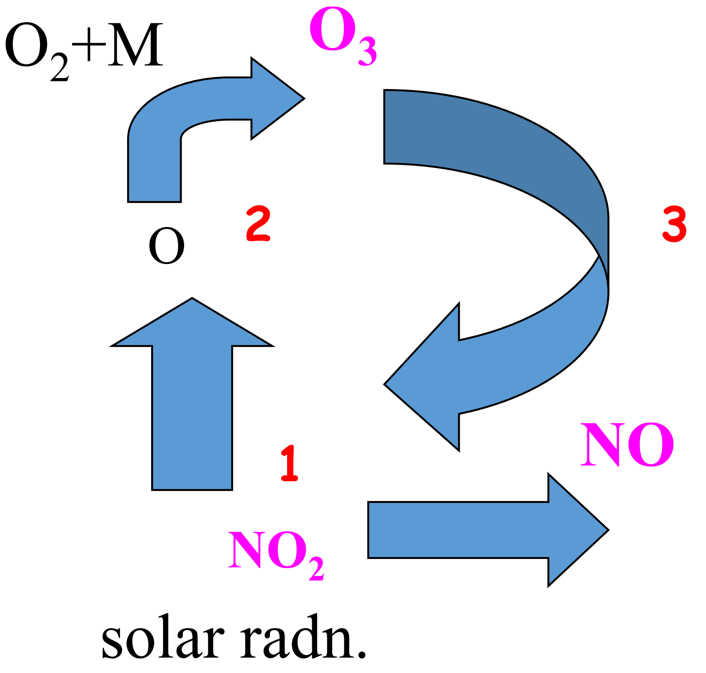
Basic Photochemical Cycle of NO_2, NO, and O_3

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. $O_3 + NO \rightarrow NO_2 + O_2$

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

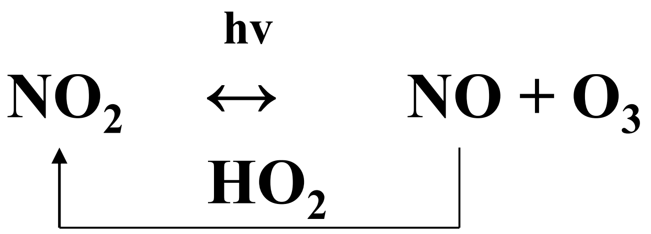


Null cycle - *cycle* **neither produces nor destroys anything overall**

NO_x/CO Cycles in Free Troposphere

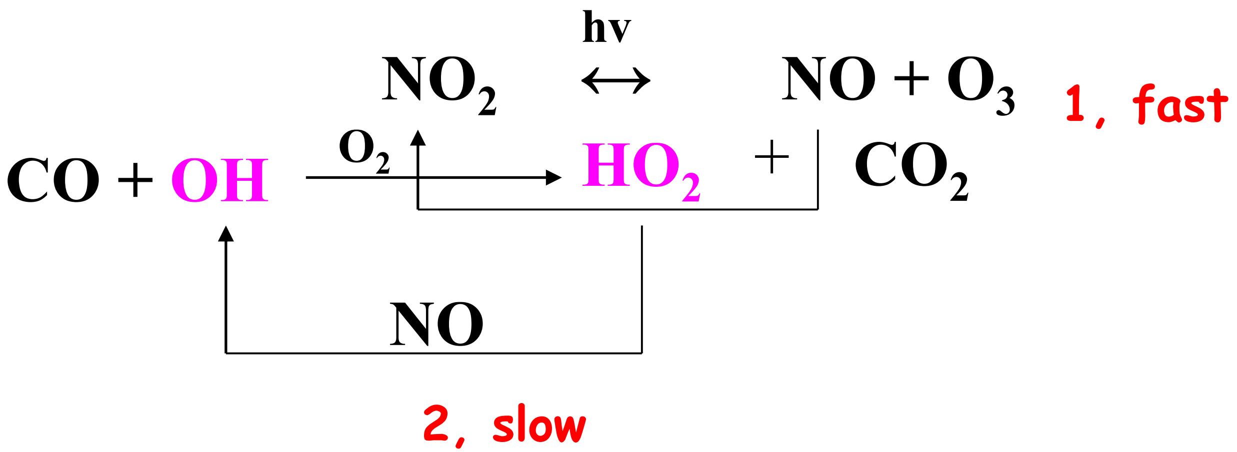
In presence of NO_x $NO_2 \overset{hv}{\leftrightarrow} NO + O_3$

In presence of CO, NO_x



$NO_2 \overset{hv}{\leftrightarrow} NO + O_3$

HO_2



$NO_2 \overset{hv}{\leftrightarrow} NO + O_3$ 1, fast

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

NO

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

Ozone Production From Methane (Jacobson, 2012)

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

$$\underset{\text{Methane}}{CH_4(g)} + \underset{\text{Hydroxyl radical}}{\dot{O}H(g)} \longrightarrow \underset{\text{Methyl radical}}{\dot{C}H_3(g)} + \underset{\text{Water vapor}}{H_2O(g)} \tag{4.16}$$

Abstraction

$$\underset{\text{Methyl radical}}{\dot{C}H_3(g)} + \underset{\text{Molecular oxygen}}{O_2(g)} \xrightarrow{M} \underset{\text{Methylperoxy radical}}{CH_3\dot{O}_2\,(g)} \tag{4.17}$$

Addition

$$\underset{\text{Nitric oxide}}{\dot{N}O(g)} + \underset{\text{Methylperoxy radical}}{CH_3\dot{O}_2(g)} \longrightarrow \underset{\text{Nitrogen dioxide}}{\dot{N}O_2(g)} + \underset{\text{Methoxy radical}}{CH_3\dot{O}(g)} \tag{4.18}$$

$$\underset{\text{Nitrogen dioxide}}{\dot{N}O_2\,(g)} + h\nu \longrightarrow \underset{\text{Nitric oxide}}{\dot{N}O(g)} + \underset{\text{Atomic oxygen}}{\cdot\dot{O}(g)} \qquad \lambda < 420\text{ nm} \tag{4.19}$$

$$\underset{\text{Ground-state atomic oxygen}}{\cdot\,\dot{O}(g)} + \underset{\text{Molecular oxygen}}{O_2(g)} \xrightarrow{M} \underset{\text{Ozone}}{O_3(g)} \tag{4.20}$$

→ 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 Production From Ethane

e-folding lifetime of C_2H_6 due to R(4.26) is 23-93 days

$$C_2H_6(g) + \dot{O}H(g) \longrightarrow \dot{C}_2H_5(g) + H_2O(g) \qquad (4.26)$$

Ethane	Hydroxyl radical	Ethyl radical	Water vapor

Abstraction

$$\dot{C}_2H_5(g) + O_2(g) \xrightarrow{M} C_2H_5\dot{O}_2(g) \qquad (4.27)$$

Ethyl radical	Molecular oxygen	Ethylperoxy radical

Addition

$$\dot{N}O(g) + C_2H_5\dot{O}_2(g) \longrightarrow \dot{N}O_2(g) + C_2H_5\dot{O}(g) \qquad (4.28)$$

Nitric oxide	Ethylperoxy radical	Nitrogen dioxide	Ethoxy radical

$$\dot{N}O_2(g) + h\nu \longrightarrow \dot{N}O(g) + \cdot\dot{O}(g) \qquad \lambda < 420\text{ nm} \qquad (4.29)$$

Nitrogen dioxide	Nitric oxide	Atomic oxygen

$$\cdot\dot{O}(g) + O_2(g) \xrightarrow{M} O_3(g) \qquad (4.30)$$

Ground-state atomic oxygen	Molecular oxygen	Ozone

→ Form O_3 via increasing the ratio of NO_2 to NO

Photochemical Smog Formation

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

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

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

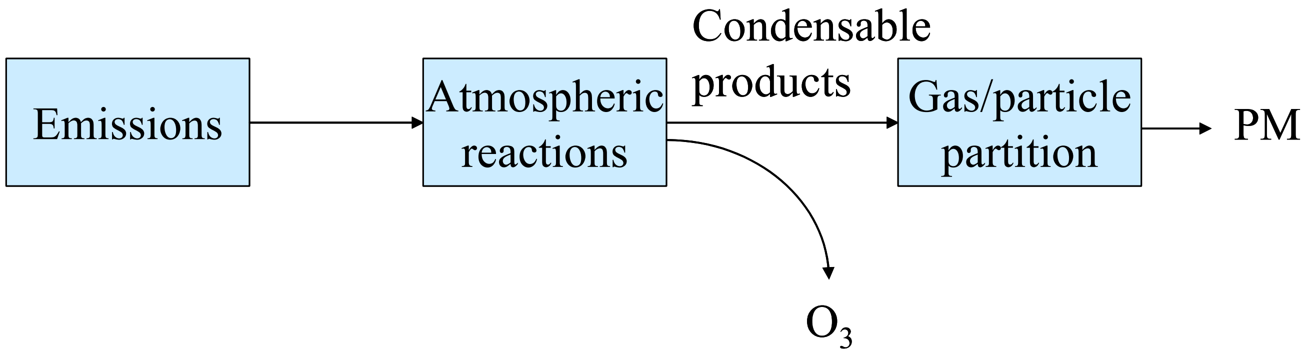
$$\underset{\text{Ground-state atomic oxygen}}{\cdot\dot{O}(g)} + \underset{\text{Molecular oxygen}}{O_2(g)} \xrightarrow{M} \underset{\text{Ozone}}{O_3(g)} \tag{4.40}$$

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)

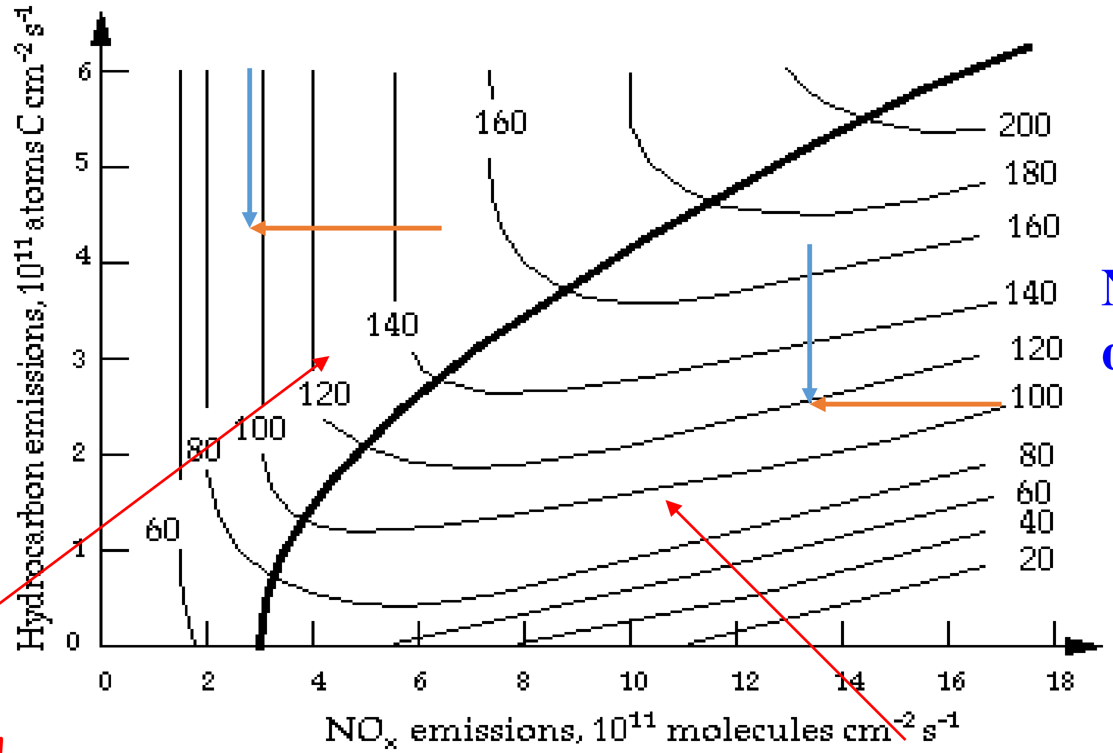
Atmospheric Biogenic VOCs

- **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.**



Ozone Isopleth

NO_x- and VOC-limited Regimes (Jacob, 1999)



Ridge line

Nonlinearity of O_3 Chemistry

NO_x limited

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

Hydrocarbon limited

$P_{O_3} = (2k_4 P_{HO_x}[RH])/(k_9[NO_2][M])$

NOx-limited: decrease VOCs,
no effect on O_3

VOC-limited: decrease NO_x,
O_3 increases

Condensed Mechanisms for Organic Chemistry used in 3-D Air Quality Models

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)

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Classification of Particles (Zhang, 2020)

Particle - Agglomerations of molecules in the liquid and / or solid phases, suspended in air. Strict – aerosol particles; broad –aerosol particles and hydrometeor particles.

- Based on atmospheric states
  - Aerosol particle: a single liquid, solid, or mix-phased particle
  - Hydrometeor particle: a single water particle suspended in or falling through the air (e.g., fog drops, cloud drops, ice crystals, snowflakes, raindrops, hailstones)
- Based on size (1 nm – 10 mm)
  - Fine ($\leq$ 2.5 μm) (Ultrafine: < 0.01-0.1 μm, submicron: < 1 μm, and supermicron: > 1 μm)
  - Coarse (> 2.5 μm) (hydrometeor: 5 μm - 8 mm)
- Based on formation mechanism
  - Primary– particles that are directly emitted into the atmosphere (e.g., black carbon, dust)
  - Secondary- particles that are formed from precursor gases in the atmosphere (e.g., sulfate, nitrate, ammonium, secondary organics)
- Based on sources
  - Anthropogenic –particles generated from anthropogenic sources (e.g., automobiles, industry, residential, agricultural)
  - Natural – particles generated from natural sources such as biogenic, dust, sea salt, forest fires

Types of Aerosol Particles

Warming effect of aerosols – the air is warmed primarily by the absorption of solar radiation by some particles. These particles include:

- **Black carbon (BC)**
- **Brown carbon (BrC) (e.g., aromatic organic compounds (OC), nitrated OC, tar balls)**
- **Soil dust components (e.g., Iron, Aluminum)**

Cooling effect of aerosols (or whitehouse effect)– the near-surface air is cooled by the backscattering incident solar radiation by some particles more than they absorb thermal-IR radiation from the Earth. These particles include:

- **Liquid water**
- **Sulfate**
- **Nitrate**
- **Ammonium**

Sources of New Particles from Emissions

Sea-spray emissions

(e.g., sea-spray, spume drops)

Volcanic eruptions

(e.g., silicate, sulfate, chloride, fluoride, water, etc)

Biomass burning

(e.g., ash, organic carbon, elemental carbon, chloride)

Wind

(e.g., pollen, dust, sea spray)

Fossil-fuel combustion

(e.g., soot, organic carbon, elemental carbon)

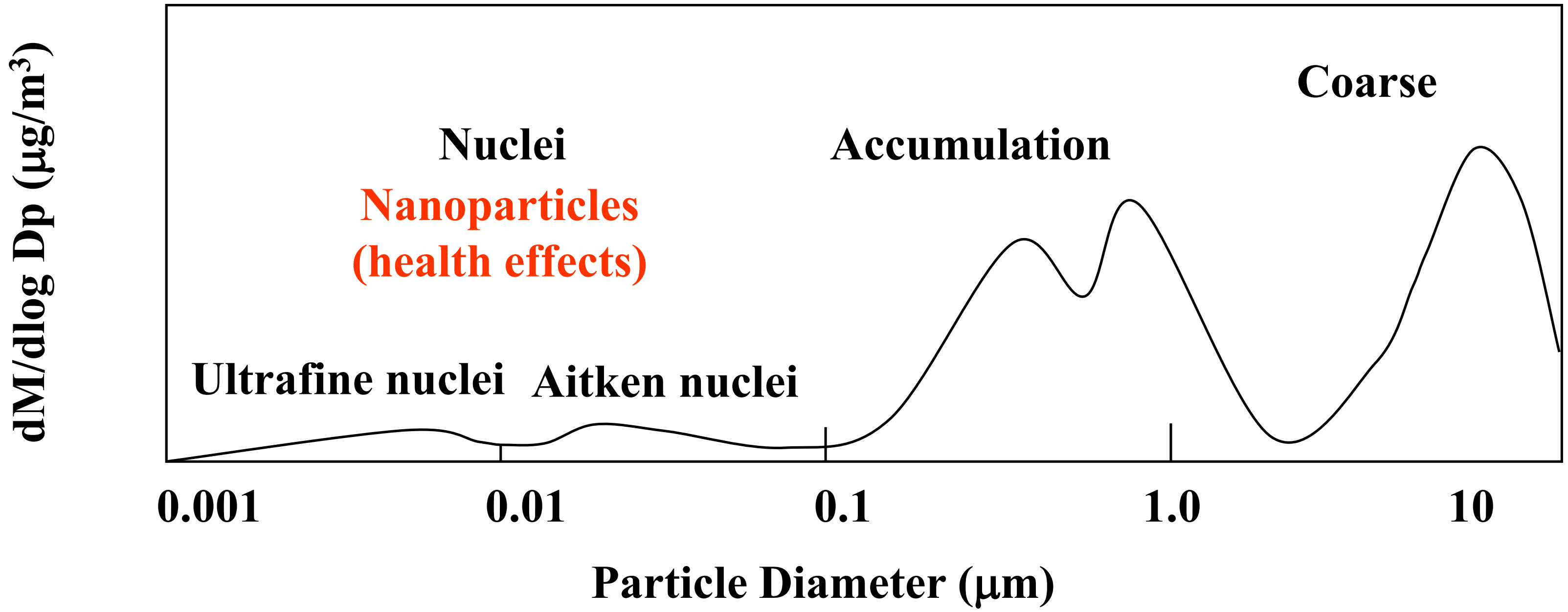
Industrial (Smelters, Oil-fired and coal-fired power plants, Municipal waste incineration, Steel-mill furnaces)

(e.g., soot, sulfate, fly ash, metals)

Miscellaneous

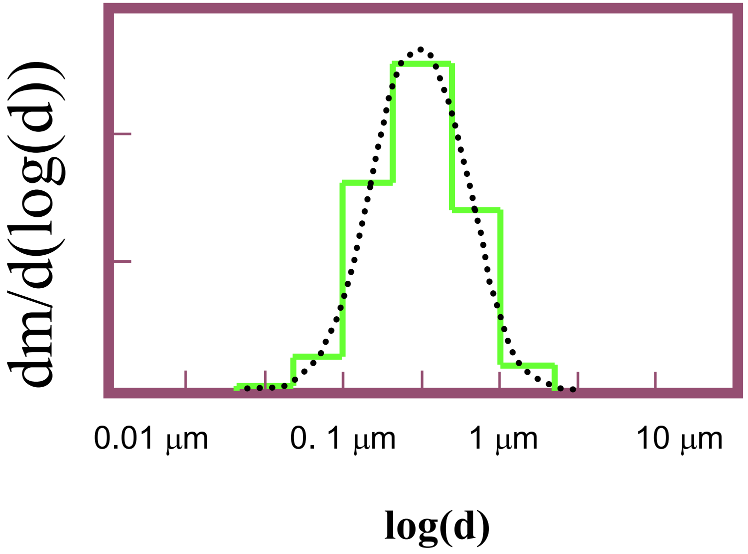
(e.g., tire rubber particles, pollen, spores, bacteria, viruses, plant debris, and meteoric debris)

Physical Characteristics of PM



Particle/drop size distribution

- Continuous representation
  - Modal distribution
  - Marshall-Palmer distribution
  - Modified Gamma distribution
- Discrete representation
  - Two-section: fine and coarse
  - Multi-sectional distribution



Regional Trends of $PM_{2.5}$ Composition

(Latest Finding on National Air Quality, EPA 454/R-07-007, 2008)

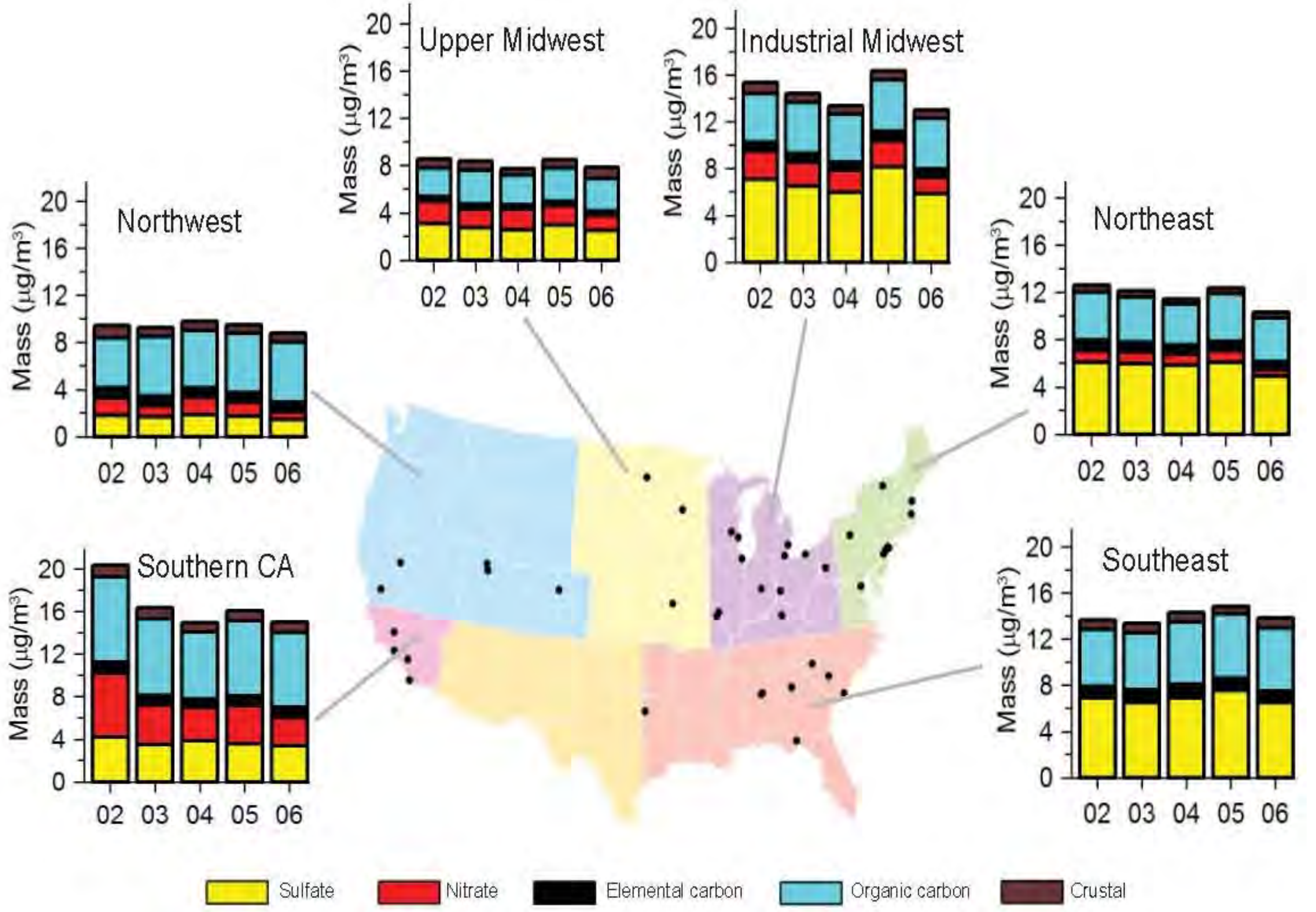


Figure 19. Regional trends in annual $PM_{2.5}$ composition in µg/m³, 2002-2006.

Note: This figure is based on 41 monitoring locations with the most complete data from the national chemical speciation network for 2002-2006. There were no sites with complete data in the Southwest. These components are presented in terms of their mass as they might have been measured by the $PM_{2.5}$ Federal Reference Method (FRM). To characterize these trends, ambient nitrate measurements, and associated ammonium, were adjusted to reflect the lower amount retained on FRM filters. Particle-bound water was included as a mass enhancement to measured sulfate, ammonium, and adjusted nitrate. Organic carbon mass was derived by material balance between measured $PM_{2.5}$ and the other components.

Sources of Particle Pollution

Component	Sources
Sulfates	Power generation
Nitrates	Cars, trucks, and power generation
Elemental and organic carbon	Cars, trucks, heavy equipment, wildfires, waste burning, and vegetation
Crustal	Suspended soil and metallurgical operations

Note: Ammonia from sources such as fertilizer and animal feed operations contributes to the formation of sulfates and nitrates that exist in the air as ammonium sulfate and ammonium nitrate. For more information about fine particle sources, visit http://www.epa.gov/air/airtrends/aqtrnd04/pm.html.

Composition of PM$_1$ at locations in Northern Hemisphere

(Q. Zhang et al., 2007)

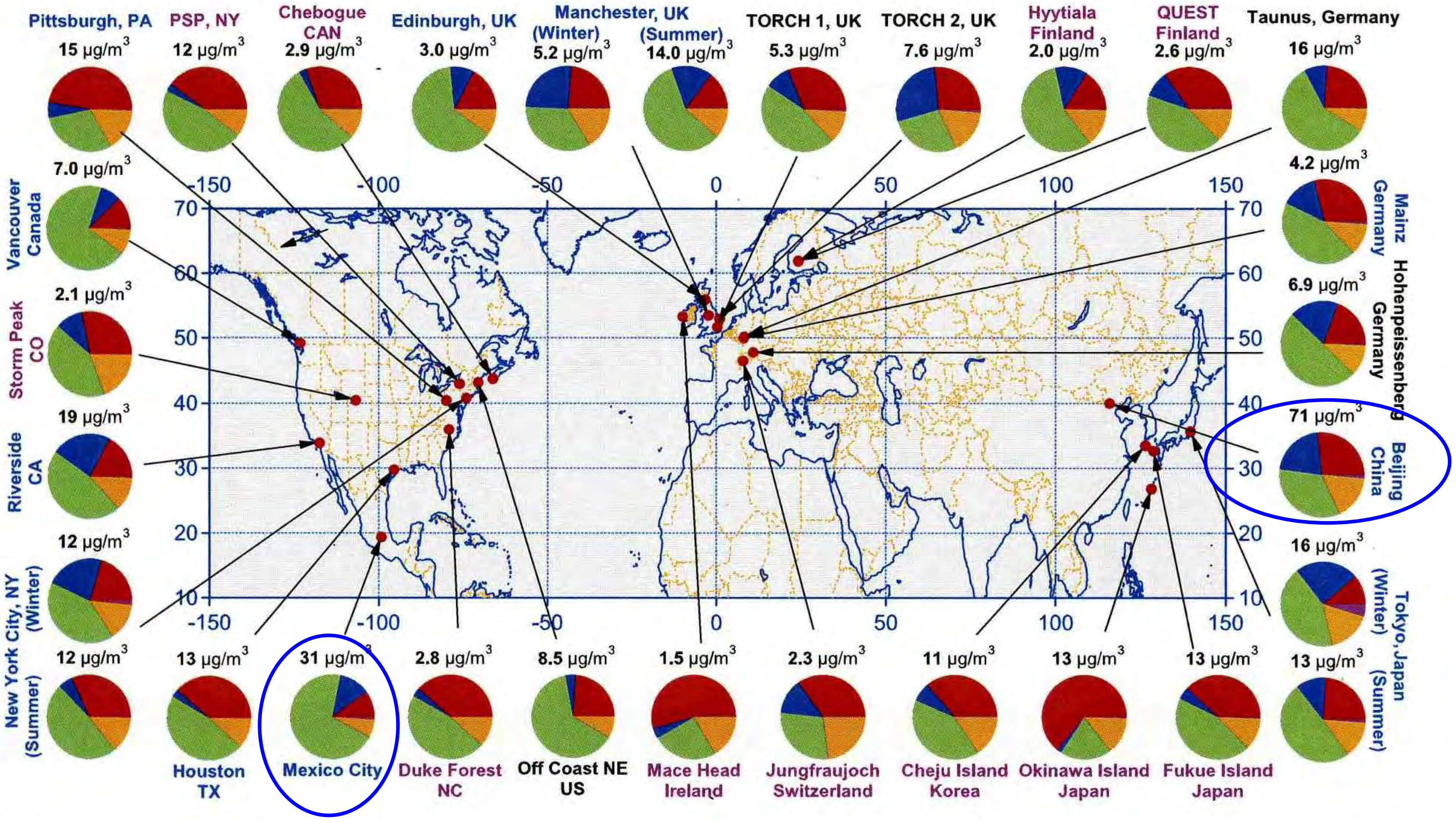
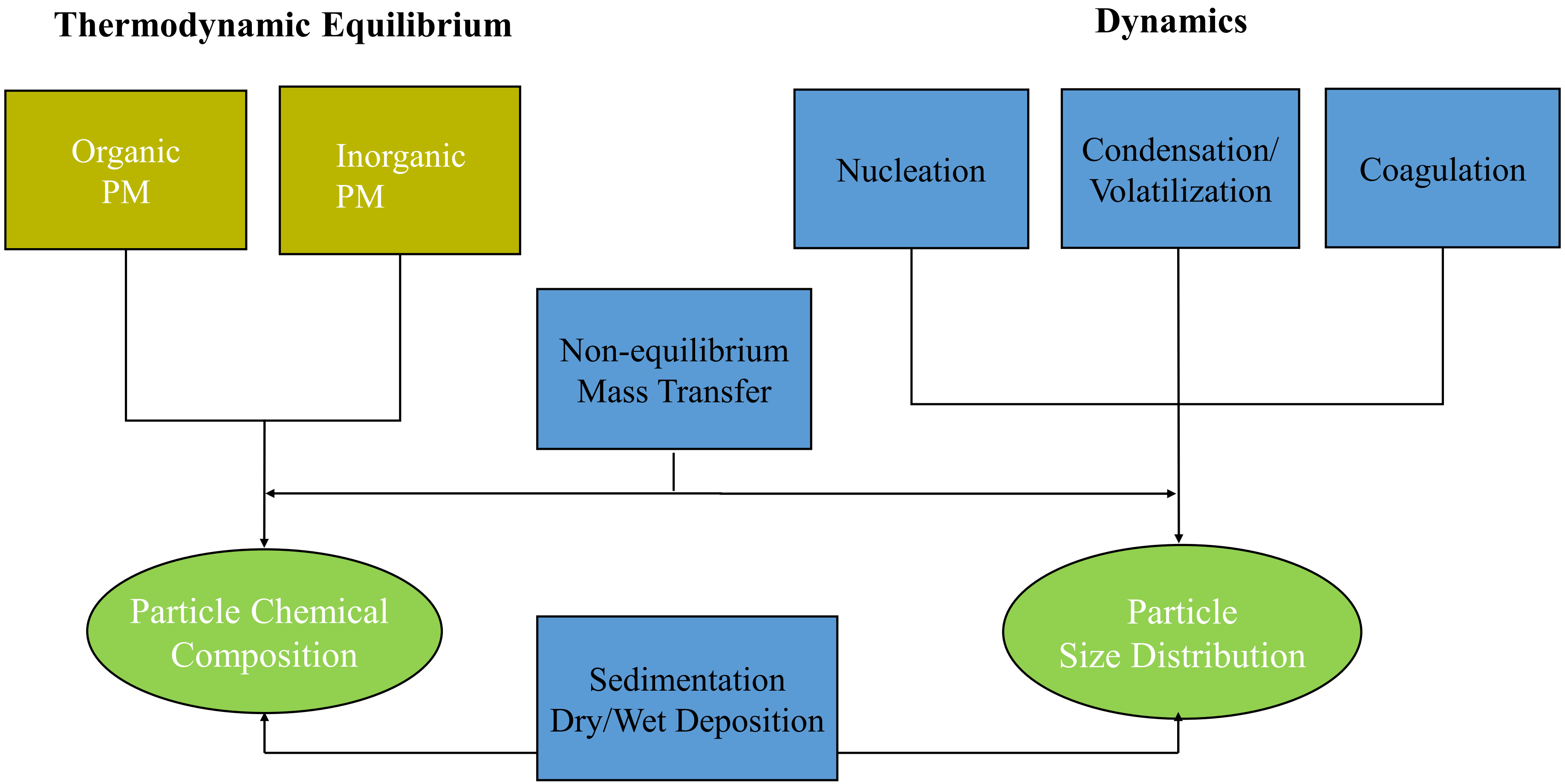


Figure 1. Location of the AMS datasets analyzed here (data shown in Table S1 in the auxiliary material). Colors for the study labels indicate the type of sampling location: urban areas (blue), <100 miles downwind of major cites (black), and rural/remote areas >100 miles downwind (pink). Pie charts show the average mass concentration and chemical composition: organics (green), sulfate (red), nitrate (blue), ammonium (orange), and chloride (purple), of NR-PM$_1$.

Thermodynamics and Dynamics of PM
(Zhang, 2020)



Thermodynamic Equilibrium

Organic PM

Inorganic PM

Dynamics

Nucleation

Condensation/ Volatilization

Coagulation

Non-equilibrium Mass Transfer

Particle Chemical Composition

Sedimentation Dry/Wet Deposition

Particle Size Distribution

Definitions of Aerosol Dynamic Processes

Nucleation is a process by which gas molecules aggregate each other or nucleate on a foreign substance or surface to form clusters that change the phase to a liquid or solid. If the radius of the cluster reaches a critical size, the cluster becomes stable and can grow further. All types of nucleation increase the volume/mass concentrations of particles, some types also increase the number concentrations of particles in the atmosphere.

Coagulation occurs when two particles collide and stick (coalesce) together. It reduces the number concentration but conserves the volume/mass concentrations of particles in the air.

Condensation/evaporation – a process in which gas molecules continuously condense (change state from gas to liquid) and liquid molecules continuously evaporate (change state from liquid to gas). Condensation increases the mass/volume concentrations but conserve the number conc. of particles in the air.

Thermodynamics and Types of Secondary PM

- Gas/Particle Equilibrium
  - » Low SVP: Irreversible gas-to-particle conversion, e.g., sulfate
  - » High SVP: Reversible gas/particle partitioning, e.g., ammonium nitrate
- Secondary PM
  - » Inorganic compounds
    - Sulfate
    - Nitrate
    - Ammonium
    - Water
  - » Organic compounds
    - EC
    - OC

Saturation vapor pressure (SVP): the partial pressure of the gas immediately over the particle's surface at the equilibrium when the mass transfer rates in both directions are equal.

S(IV) and S(VI) Families

(Jacobson, 2012)

S(IV) Family		S(VI) Family	
Chemical Name	Chemical Formula	Chemical Name	Chemical Formula
Sulfur dioxide	$SO_2(g,aq)$		
Sulfurous acid	$H_2SO_3(aq)$	Sulfuric acid	$H_2SO_4(g,aq)$
Bisulfite ion	HSO_3^-	Bisulfate ion	HSO_4^-
Sulfite ion	SO_3^{2-}	Sulfate ion	SO_4^{2-}

Table 10.1

Gas-Phase Oxidation of S(IV) to S(VI)
(Jacobson, 2012)

Three-step process:

(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.**

$$\underset{\text{Sulfur dioxide}}{SO_2(g)} \xrightarrow{+\dot{O}H(g),\ M} \underset{\text{Bisulfite}}{H\dot{S}O_3(g)} \xrightarrow[H\dot{O}_2(g)]{+\ O_2(g)} \underset{\text{Sulfur trioxide}}{SO_3(g)} \xrightarrow{+\ H_2O(g)} \underset{\text{Sulfuric acid}}{H_2SO_4(g)} \qquad (10.9)$$

$$\underset{\text{Sulfuric acid gas}}{H_2SO_4(g)} \longrightarrow \underset{\text{Dissolved sulfuric acid}}{H_2SO_4(aq)} \rightleftharpoons \underset{\text{Hydrogen ion}}{H^+} + \underset{\text{Bisulfate ion}}{HSO_4^-} \rightleftharpoons \underset{\text{Hydrogen ion}}{2H^+} + \underset{\text{Sulfate ion}}{SO_4^{2-}} \qquad (10.6)$$

This is a dominant mechanism to produce S(VI) in aerosol particles, particularly when RH < 70%.

Aqueous-Phase Oxidation of S(IV) to S(VI) (1)

(Jacobson, 2012)

Three-step process:

(1) Dissolution of SO_2 (g) into liquid-water drops to produce SO_2(aq);
(1) 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.

This is a dominant mechanism to produce S(VI) in cloud/rain drops.

Production of Nitric Acid and Nitrate
(Jacobson, 2012)

Nitric acid deposition occurs in and downwind of urban areas and is enhanced by the presence of clouds or fogs.

$$\dot{O}H(g) + \dot{N}O_2(g) \xrightarrow{M} HNO_3(g) \qquad (10.14)$$

Hydroxyl radical	Nitrogen dioxide	Nitric acid

$$HNO_3(g) \rightleftharpoons HNO_3(aq) \rightleftharpoons H^+ + NO_3^- \qquad (10.7)$$

Nitric acid gas	Dissolved nitric acid	Hydrogen ion	Nitrate ion

Chemical Reactions in Atmospheric Aerosols (Seinfeld and Pandis, 2016)

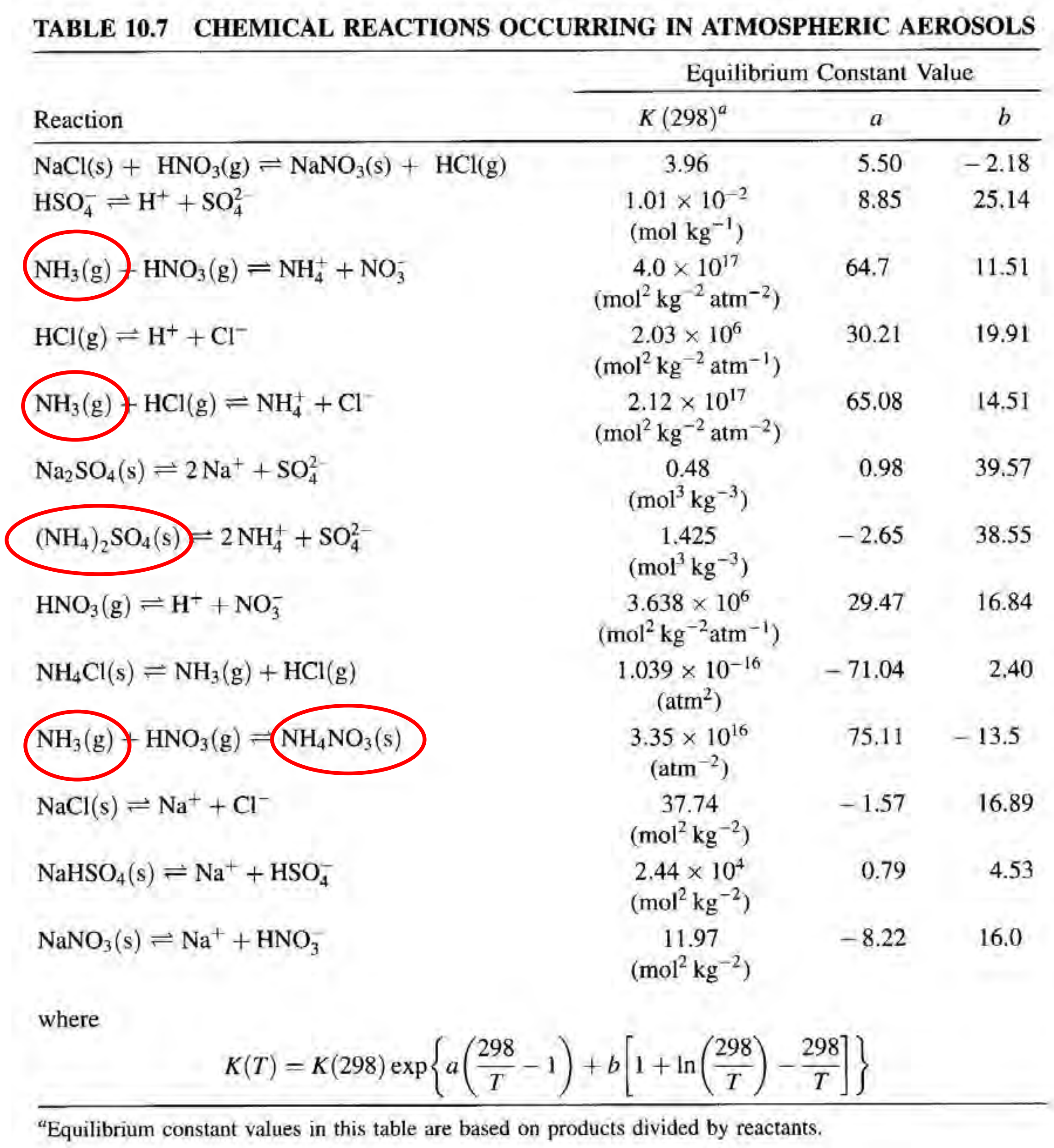


TABLE 10.7 CHEMICAL REACTIONS OCCURRING IN ATMOSPHERIC AEROSOLS

	Equilibrium Constant Value		
Reaction	K (298)[a]	a	b
$NaCl(s) + HNO_3(g) \rightleftharpoons NaNO_3(s) + HCl(g)$	3.96	5.50	−2.18
$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$	1.01×10^{-2} (mol kg^{-1})	8.85	25.14
$NH_3(g) + HNO_3(g) \rightleftharpoons NH_4^+ + NO_3^-$	4.0×10^{17} (mol^2 kg^{-2} atm^{-2})	64.7	11.51
$HCl(g) \rightleftharpoons H^+ + Cl^-$	2.03×10^6 (mol^2 kg^{-2} atm^{-1})	30.21	19.91
$NH_3(g) + HCl(g) \rightleftharpoons NH_4^+ + Cl^-$	2.12×10^{17} (mol^2 kg^{-2} atm^{-2})	65.08	14.51
$Na_2SO_4(s) \rightleftharpoons 2\,Na^+ + SO_4^{2-}$	0.48 (mol^3 kg^{-3})	0.98	39.57
$(NH_4)_2SO_4(s) \rightleftharpoons 2\,NH_4^+ + SO_4^{2-}$	1.425 (mol^3 kg^{-3})	−2.65	38.55
$HNO_3(g) \rightleftharpoons H^+ + NO_3^-$	3.638×10^6 (mol^2 kg^{-2}atm^{-1})	29.47	16.84
$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$	1.039×10^{-16} (atm^2)	−71.04	2.40
$NH_3(g) + HNO_3(g) \rightleftharpoons NH_4NO_3(s)$	3.35×10^{16} (atm^{-2})	75.11	−13.5
$NaCl(s) \rightleftharpoons Na^+ + Cl^-$	37.74 (mol^2 kg^{-2})	−1.57	16.89
$NaHSO_4(s) \rightleftharpoons Na^+ + HSO_4^-$	2.44×10^4 (mol^2 kg^{-2})	0.79	4.53
$NaNO_3(s) \rightleftharpoons Na^+ + HNO_3^-$	11.97 (mol^2 kg^{-2})	−8.22	16.0

where

$$K(T) = K(298)\exp\left\{a\left(\frac{298}{T} - 1\right) + b\left[1 + \ln\left(\frac{298}{T}\right) - \frac{298}{T}\right]\right\}$$

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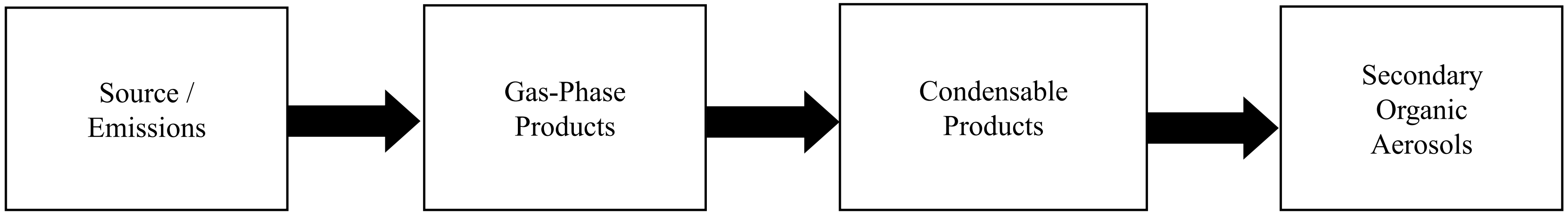
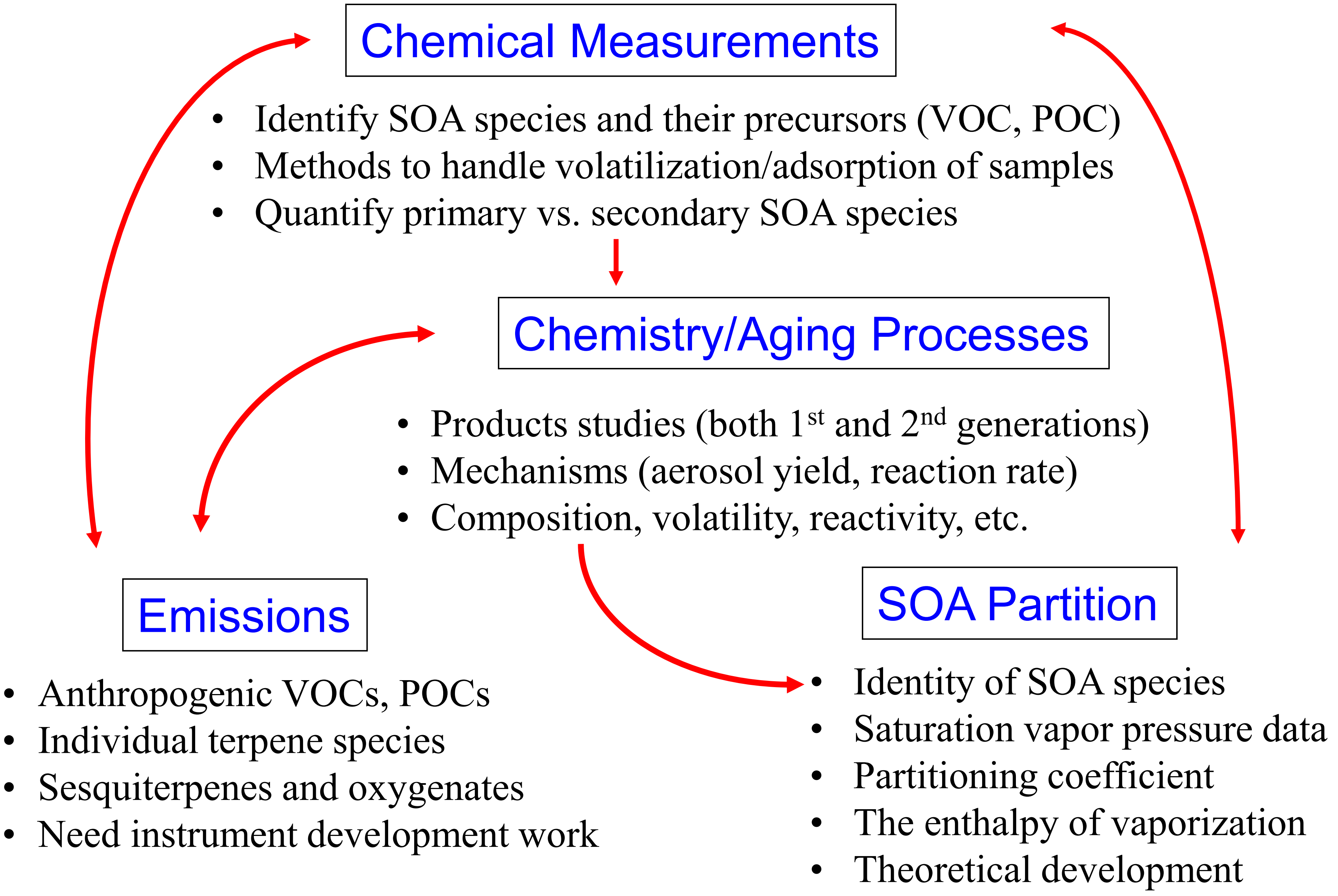
[a] Equilibrium constant values in this table are based on products divided by reactants.

Formation of Secondary Organic Aerosols (Zhang, 2020)



- **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)**

SOA Formation: Knowledge Gaps and Data Needs (Zhang, 2020)



Chemical Measurements

- Identify SOA species and their precursors (VOC, POC)
- Methods to handle volatilization/adsorption of samples
- Quantify primary vs. secondary SOA species

Chemistry/Aging Processes

- Products studies (both 1st and 2nd generations)
- Mechanisms (aerosol yield, reaction rate)
- Composition, volatility, reactivity, etc.

Emissions

- Anthropogenic VOCs, POCs
- Individual terpene species
- Sesquiterpenes and oxygenates
- Need instrument development work

SOA Partition

- Identity of SOA species
- Saturation vapor pressure data
- Partitioning coefficient
- The enthalpy of vaporization
- Theoretical development

Outline

- Importance of Atmospheric Chemistry and Aerosol
- Tropospheric Gas-Phase Chemistry
  - Chemistry of NOx, CO, VOCs, and O_3
  - Gas-phase chemical mechanisms used in CW-AQF models
- Atmospheric Aerosol
  - Classification and sources
  - Size distribution and chemical composition
  - Thermodynamics and dynamic processes
  - Formation mechanisms of secondary inorganic and organic aerosol
- **Major Issues In O_3 and $PM_{2.5}$ Pollution Control**
- **Summary**

Sources: Zhang et al. (2012a, b), Zhang and Baklanov (2019), and Zhang (2015) and (2020)

Major Issues In O_3 and $PM_{2.5}$ Pollution Control

- **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

Summary

- O_3, PM, acid deposition, and other air pollutants are produced through gas-phase, aqueous-phase, and heterogeneous chemical reactions. Key atmospheric radical are HO, HO_2, and RO_2 that oxidize NO_x and VOCs to form O_3 and PM.
- O_3 concentrations depend upon solar actinic flux and the ratio of NO_2 to NO. Realistically accurate emissions inventories of NO_x and VOCs are critical for CW-AQF using AQMs.
- NH_3 emissions react with the atmospheric acids to produce inorganic aerosols. If inorganic PM are to be forecasted, the emissions inventory of NH_3 and SO_2 is important for inorganic PM forecasting. The oxidation products of VOCs can form secondary organic aerosol.
- 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.
- Atmospheric aerosols are made of multiple inorganic and organic chemical compounds. Their size ranges from a few nanometers to tens of micrometers. The most commonly used aerosol size distribution representations in CW-AQF are the sectional and the modal size distributions. The sectional size representation that can simulate both particle mass and number accurately is recommended for AQF.
- Aerosol processes include thermodynamic equilibrium and dynamic processes such as nucleation, condensation/evaporation, coagulation, and gas-particle mass transfer. A number of aerosol modules with varying degrees of complexity have been implemented in CW-AQF models to represent these processes. Aerosol forecast may vary with different aerosol modules.

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