AP 3050 Air Pollution

Air Pollution and Global Warming: History, Science, and Solutions

Chapter 4: Aerosol Particles in the Polluted and Global Atmosphere

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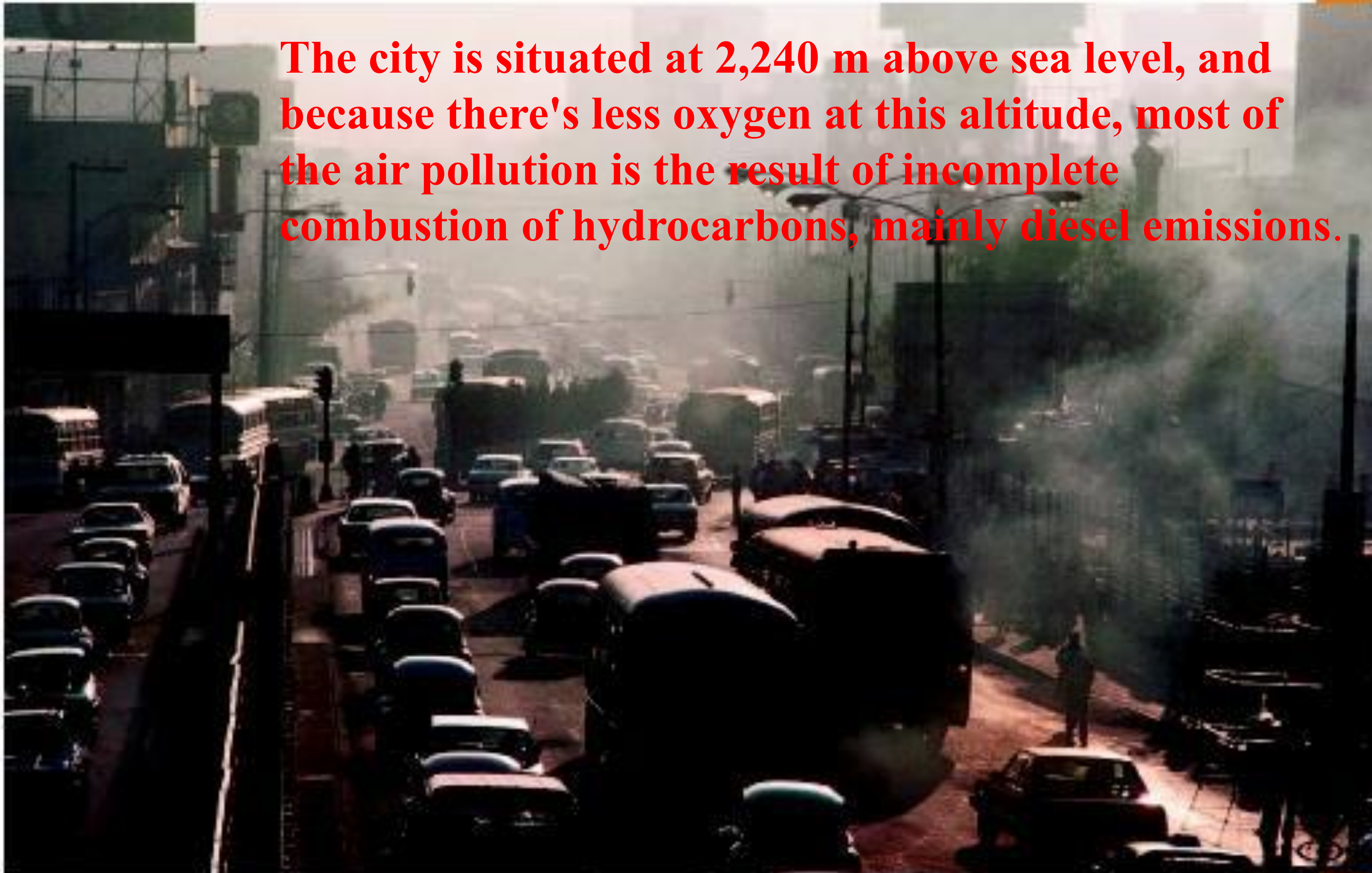
Spring 2021

By Mark Z. Jacobson
Cambridge University Press (2012)

Winter inversion – Dec ~ Feb

Salt Lake City

Rush Spedden; rmcleanair.blogspot.com/2007/01/utah-choking-on-pollution.html



Mexico City

Stephanie Maze/www.pollutionissues.com/Ve-Z/Vehicular-Pollution.html

Sao Paulo

upload.wikimedia.org/wikipedia/commons/6/6b/Zona_Leste_-_São_Paulo-Brasil.jpg

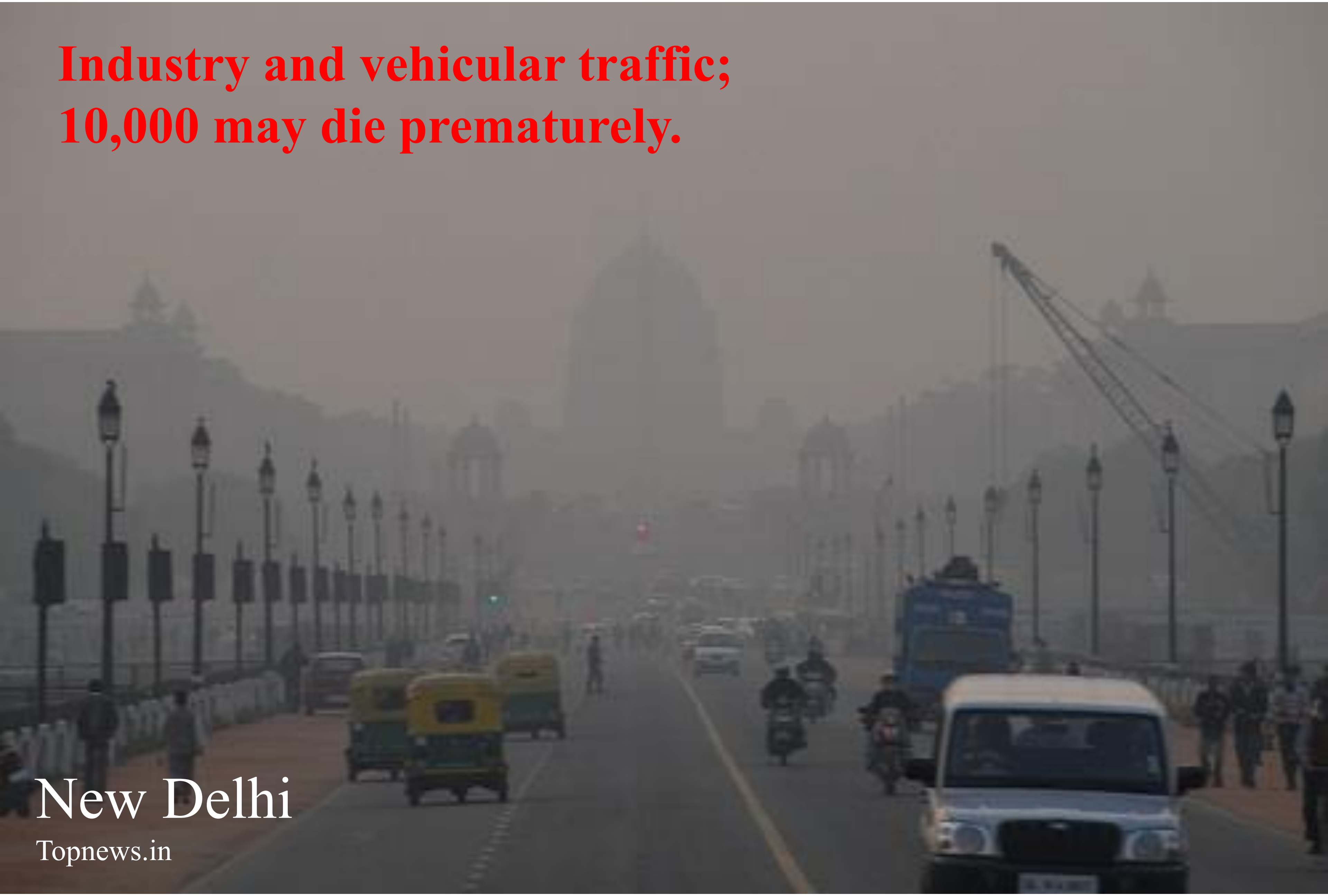
Air pollution in São Paulo kills more people than car accidents, breast cancer, and AIDS combined.

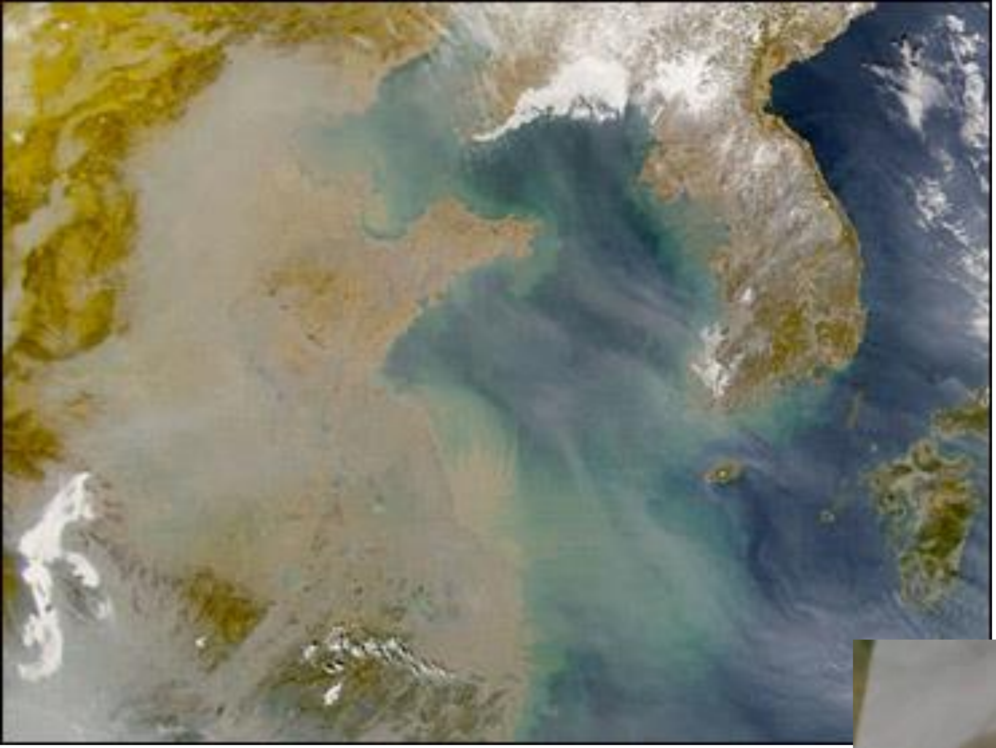
20 M people, 7 M cars!

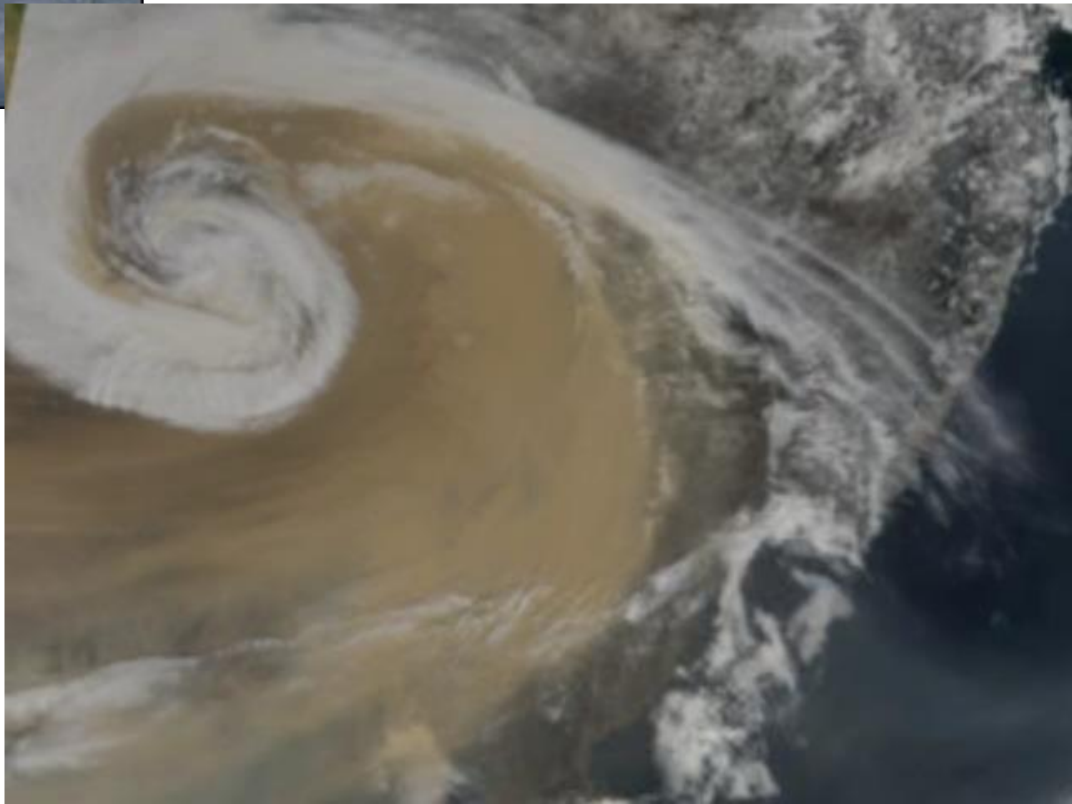
San Paulo

(http://reachingbrazil.blogspot.tw)


Beijing
Chinadaily.com.cn


Industry and vehicular traffic;
10,000 may die prematurely.
New Delhi
Topnews.in





Asian Brown Cloud

NASA Satellite Images

Particle Characteristics

Mode	Diameter (μm)	Number (#/cm^3)
Gas molecules	0.0005	2.45×10^{19}
Aerosol particles		
Small	< 0.1	10^3-10^6
Medium	0.1-2.5	1-10^4
Large	2.5-8000	<1 - 10
Hydrometeor particles		
Fog drops	5-20	1-500
Cloud drops	10-200	1-1000
Drizzle	200-1000	0.01-1
Raindrops	1000-8000	0.001-0.01
Hail	5000-115,000	0.0001-0.001

Particle Size Distribution (PSD)

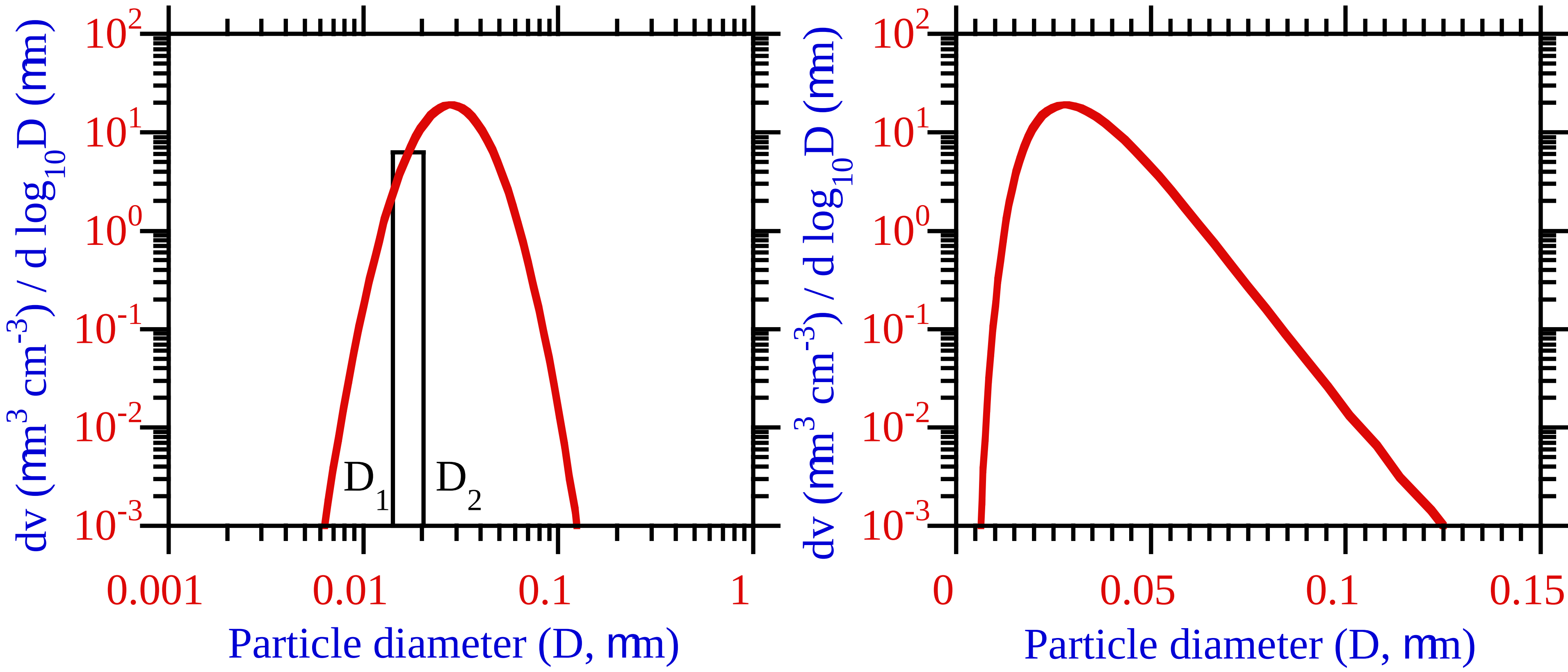
Variation of particle concentration (i.e., number, surface area, volume, or mass of particles per unit volume of air) with size.

Size distribution usually divided into modes:

Mode	Diameter Range (nm)
Nucleation	< 100
Submode 1	<10
Submode 2	10-100
Accumulation	100 – 2500
Submode 1	~ 200
Submode 2	~ 500-700
Coarse	> 2500

Lognormal Distribution

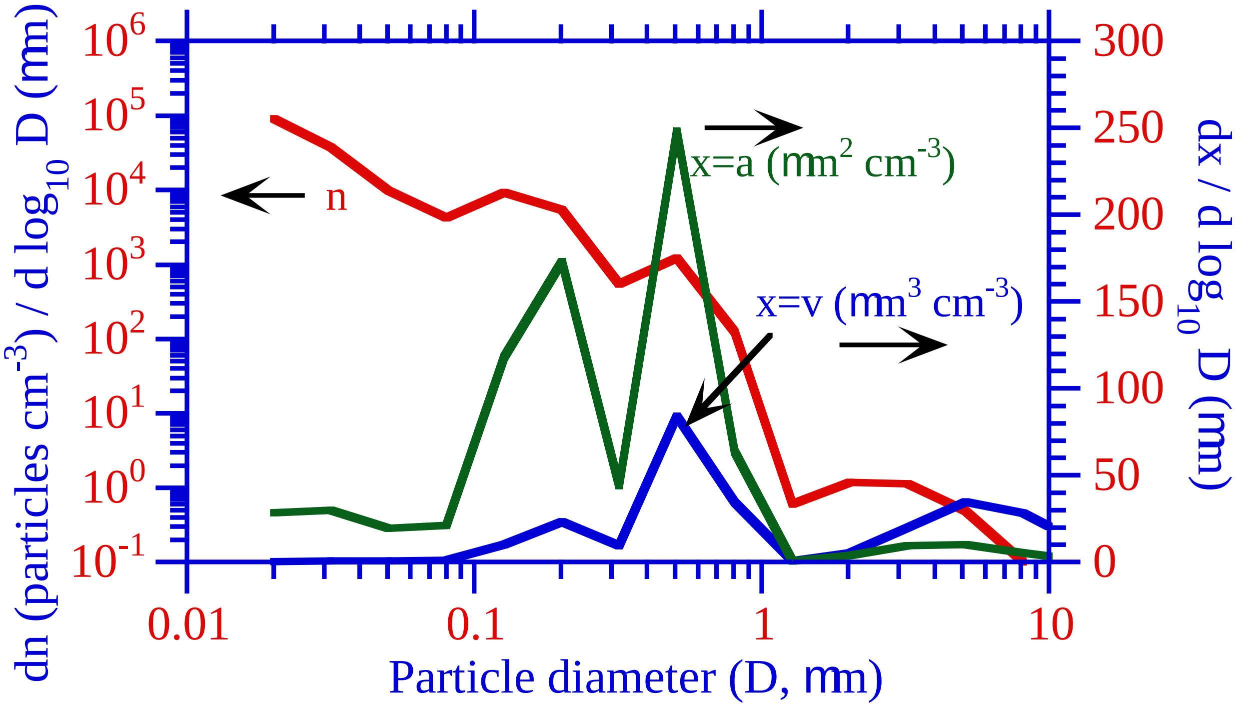
Describes an individual mode of a size distribution



Ambient Size Distribution

Claremont, California,
Aug., 1987

Mode	Diameter Range (nm)
Nucleation	< 100
Accumulation	100-2500
-Submode 1	~ 200
-Submode 2	~ 500-700
Coarse	> 2500



Major Particle Emission Sources

Sea spray
Soil dust
Volcanoes
Biomass burning
Fossil-fuel combustion
Industrial
Miscellaneous

Sea Spray Emission

Form when winds and waves force air bubbles to burst at sea surface. Contain composition of sea water

- **Spume drops**

  Drops larger than sea spray form when winds tear off wave crests.

- **Sea-spray acidification**

  Reduction in chloride in sea spray drops as sulfuric acid or nitric acid enter the drops.

- **Dehydration**

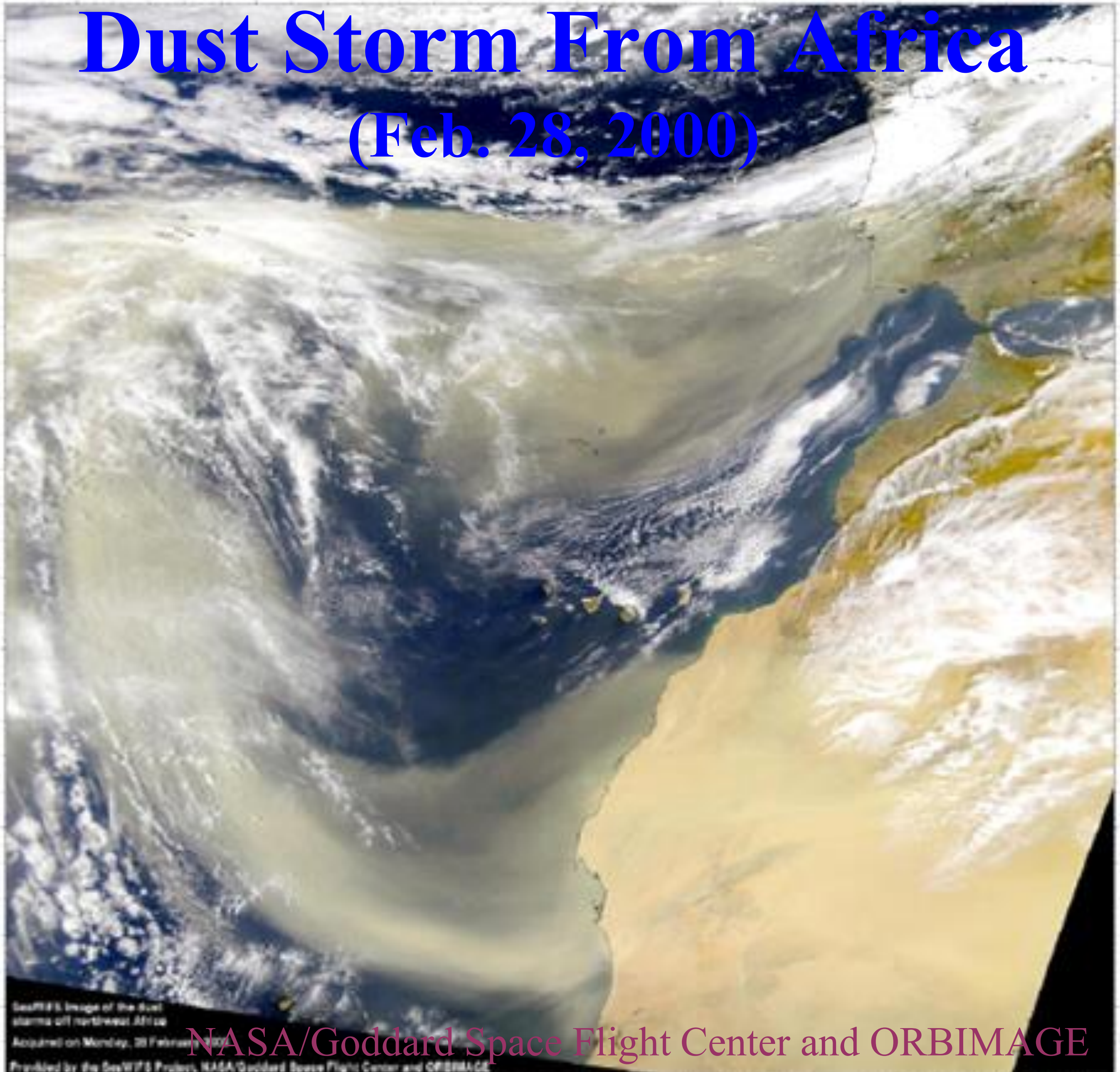
  Water loss when drop evaporates in low relative-humidity air.

Constituents of Sea Water

Constituent	Mass percent
Water	96.78
Sodium	1.05
Chlorine	1.88
Magnesium	0.125
Sulfur	0.0876
Calcium	0.0398
Potassium	0.0386
Carbon	0.0027

Table 5.3

Dust Storm From Africa
(Feb. 28, 2000)



NASA/Goddard Space Flight Center and ORBIMAGE

Breakdown of Rocks to Soil

- **Physical weathering**

  Disintegration of rocks and minerals by processes not involving chemical reactions. Examples: when stress applied to a rock. Stresses arise due to high pressure under soil or when rocks freeze/thaw or when saline solutions enter cracks and cause disintegration/fracture.

- **Chemical weathering**

  Disintegration of rocks and minerals by chemical reaction. Example: Dissolution of gypsum in water:

$$CaSO_4\text{-}2H_2O(s) \rightleftharpoons Ca^{2+} + SO_4^{2-} + 2H_2O(aq) \quad (5.1)$$

Calcium sulfate dihydrate (gypsum) — Calcium ion — Sulfate ion — Liquid water

Types of Minerals in Soil Dust

Quartz - SiO_2(s) - clear, colorless, resistant to chemical weathering

Feldspars (長石) - 50 percent of rocks on Earth's surface

- Potassium feldspar - $KAlSi_3O_3$(s)
- Plagioclase feldspar - $NaAlSi_3O_3$-$CaAl_2Si_2O_8$(s)

Hematite (赤鐵礦) - Fe_2O_3(s) - reddish brown

Calcite (方解石) - $CaCO_3$(s) - found in limestone

Dolomite (白雲石) - $CaMg(CO_3)_2$(s)

Gypsum (石膏) - $CaSO_4$-$2H_2O$(s)- colorless to white

Clays - soft, compact, odorous minerals resulting from weathering

- Kaolinite - $Al_4Si_4O_{10}(OH)_8$(s)
- Illite
- Smectite
- Vermiculite
- Chlorite

Organic matter - plant litter or animal tissue broken by bacteria

Time For Particles to Fall 1 km

Diam. (μm)	Time to Fall 1 km
0.02	228 y
0.1	36 y
1.0	328 d
10	3.6 d
100	1.1 h
1000	4 m
5000	1.8 m

Only particles smaller than 10 μm reach the global atmosphere.

Sarychev, Kuril Islands (June, 2009)

NASA Johnson Space Center

Volcanic Emission

Over 500 volcanos are currently active.

Magma contains 1-4 percent gas by mass.

Water vapor makes up 50-80 percent of gas mass

Some other constituents:

$CO_2(g)$	$SO_2(g)$
$OCS(g)$	$N_2(g)$
$CO(g)$	$H_2(g)$
$S_2(g)$	$HCl(g)$
$Cl_2(g)$	$F_2(g)$

Particles

Most abundant are silicate minerals.

Range in size from <0.1 to 100 μm

Savannah Fire, Masai Mara, Kenya


EricIsselee/Dreamstime.com

Grass Fire, Feb. 28, 2009

Fairiegoodmother/Dreamstime.com

Biomass-Burning Emission

- Burning of evergreen forests, deciduous forests, woodlands, grasslands, agricultural land either to clear land, stimulate grass growth, manage forest growth, or satisfy a ritual.

- Gas constituents

  $CO(g)$ $CO_2(g)$
  $CH_4(g)$ $NO_x(g)$
  ROG $SO_2(g)$

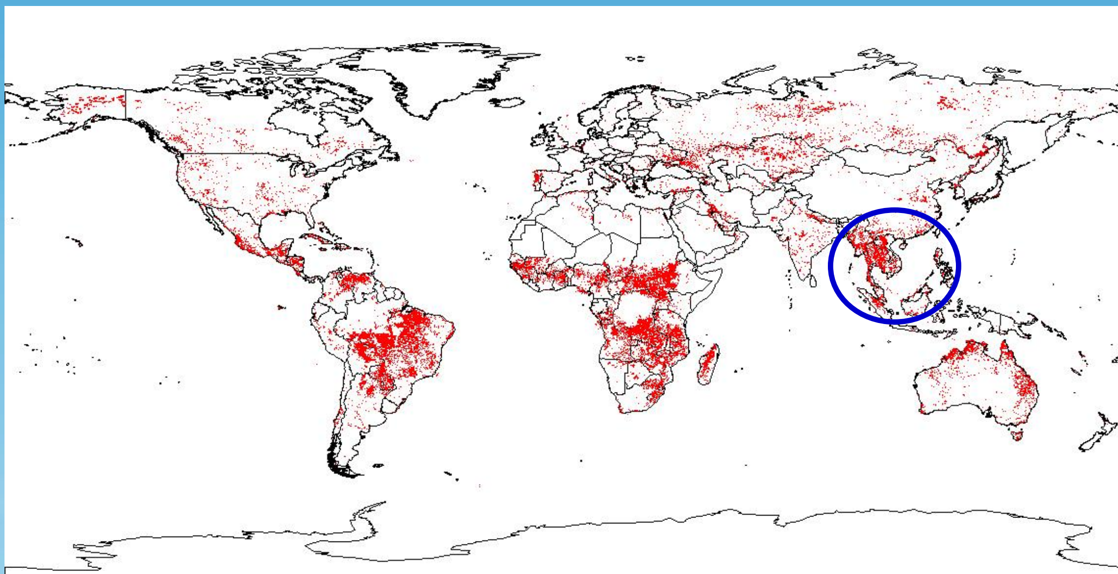
- Particle constituents

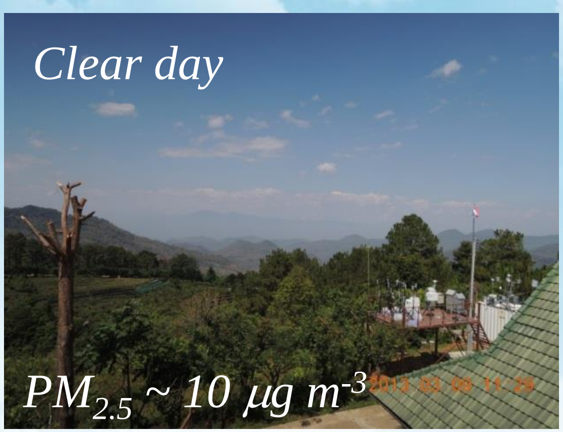
  Ash, plant fibers, soil dust, organic matter, soot (black carbon plus organic matter)

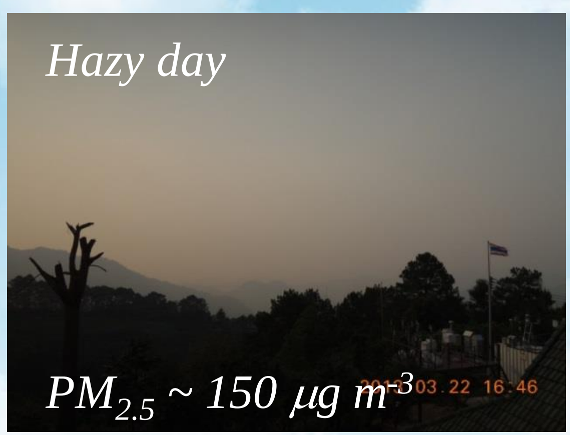
- Composition of soot

  High temperatures --> high ratio of BC:OM in soot

Biomass-burning haze in SEA







Fossil Fuels

- **Coal**

  Combustible brown-to-black carbonaceous sedimentary rock formed by compaction of partially decomposed plant material.

  Stages of coal metamorphosis

  Peat (unconsolidated, brown-black)

  Peat coal (consolidated, brown-black) 泥煤

  Lignite coal (brown-black) 褐煤

  Bituminous (soft) coal (dark brown to black) 煙煤

  Anthracite (hard) coal (black) 無煙煤

- **Oil (petroleum)**

  Natural greasy, viscous, combustible hydrocarbon liquid that forms from geological-scale decomposition of plants and animals.

Fossil-Fuel Combustion Emission

- **Gases**

  $NO_x(g)$, ROG(g), CO(g), $CO_2(g)$, $CH_4(g)$, $SO_2(g)$

- **Particles**

  Soot (BC+OM), OM alone, SO_4^{2-}, metals, fly ash

- **Fly ash**

  Contains O, Si, Al, Fe, Ca, Mg.

Fossil-Fuel Soot Emissions

Srecko/Kenneth Sponsler/Efired/Dreamstime.com.

Industrial Emission

Source	Metals in Fly Ash
Smelters	Fe, Cd, Zn
Oil-fired power plants	V, Ni, Fe
Coal-fired power plants	Fe, Zn, Pb, V, Mn, Cr, Cu, Ni, As, Co, Cd, Sb, Hg
Municipal waste incineration	Zn, Fe, Hg, Pb, Sn, As, Cd, Co, Cu, Mn, Ni, Sb
Steel-mill furnaces	Fe, Zn, Cr, Cu, Mn, Ni, Pb

Table 5.5

Miscellaneous Particle Sources

Tire-rubber particles
Pollen
Spores
Bacteria
Viruses
Plant debris
Meteoric debris

Processes Affecting Particle Evolution

- Emission
- Homogeneous nucleation
- Coagulation
- Growth

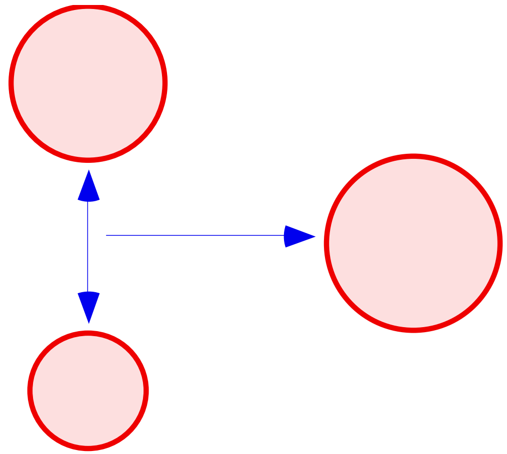
  Condensation/evaporation

  Deposition/sublimation

  Dissolution, dissociation, hydration

  Solid precipitation
- Dry deposition
- Sedimentation
- Rainout
- Washout

Coagulation



$$\frac{\partial n_{\upsilon}}{\partial t} = \frac{1}{2}\int_{0}^{\upsilon} \beta_{\upsilon-\bar{\upsilon},\bar{\upsilon}}\, n_{\upsilon-\bar{\upsilon}}\, n_{\bar{\upsilon}}\, d\bar{\upsilon} - n_{\upsilon}\int_{0}^{\infty} \beta_{\upsilon,\bar{\upsilon}}\, n_{\bar{\upsilon}}\, d\bar{\upsilon} \qquad (5.2)$$

Coagulation

Occurs when two particles collide and stick together (coalesce).
Reduces number concentration but conserves volume concentration

Classic coagulation mechanisms

- Brownian motion
- Convective Brownian diffusion enhancement
- Gravitational collection
- Turbulent inertial motion
- Turbulent shear

Additional mechanisms

- Diffusiophoresis
- Thermophoresis
- Electric charge
- van der Waals forces
- Fractal geometry effects

Effect of Brownian Coagulation

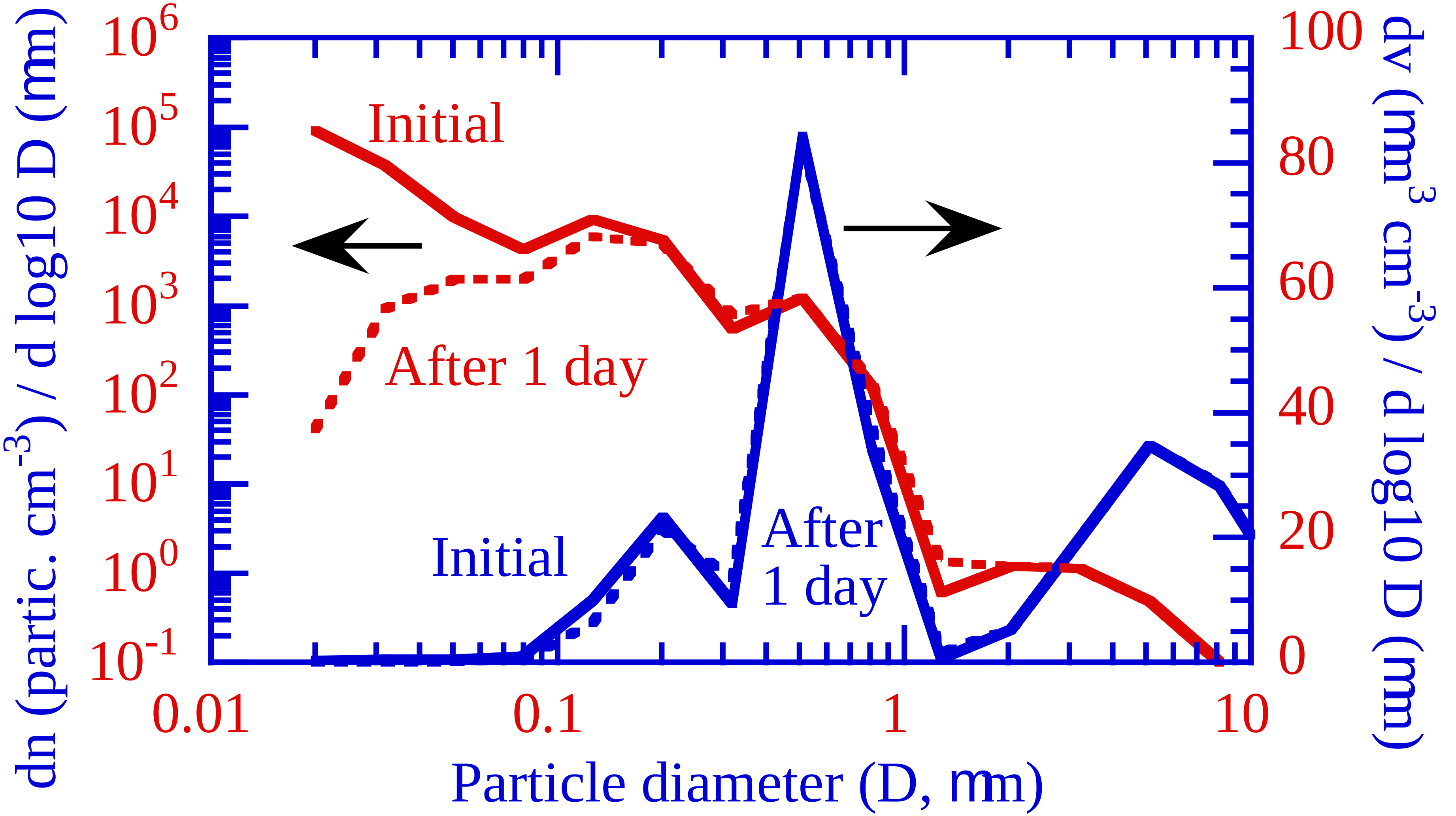


Figure 5.10

Condensation/Evaporation

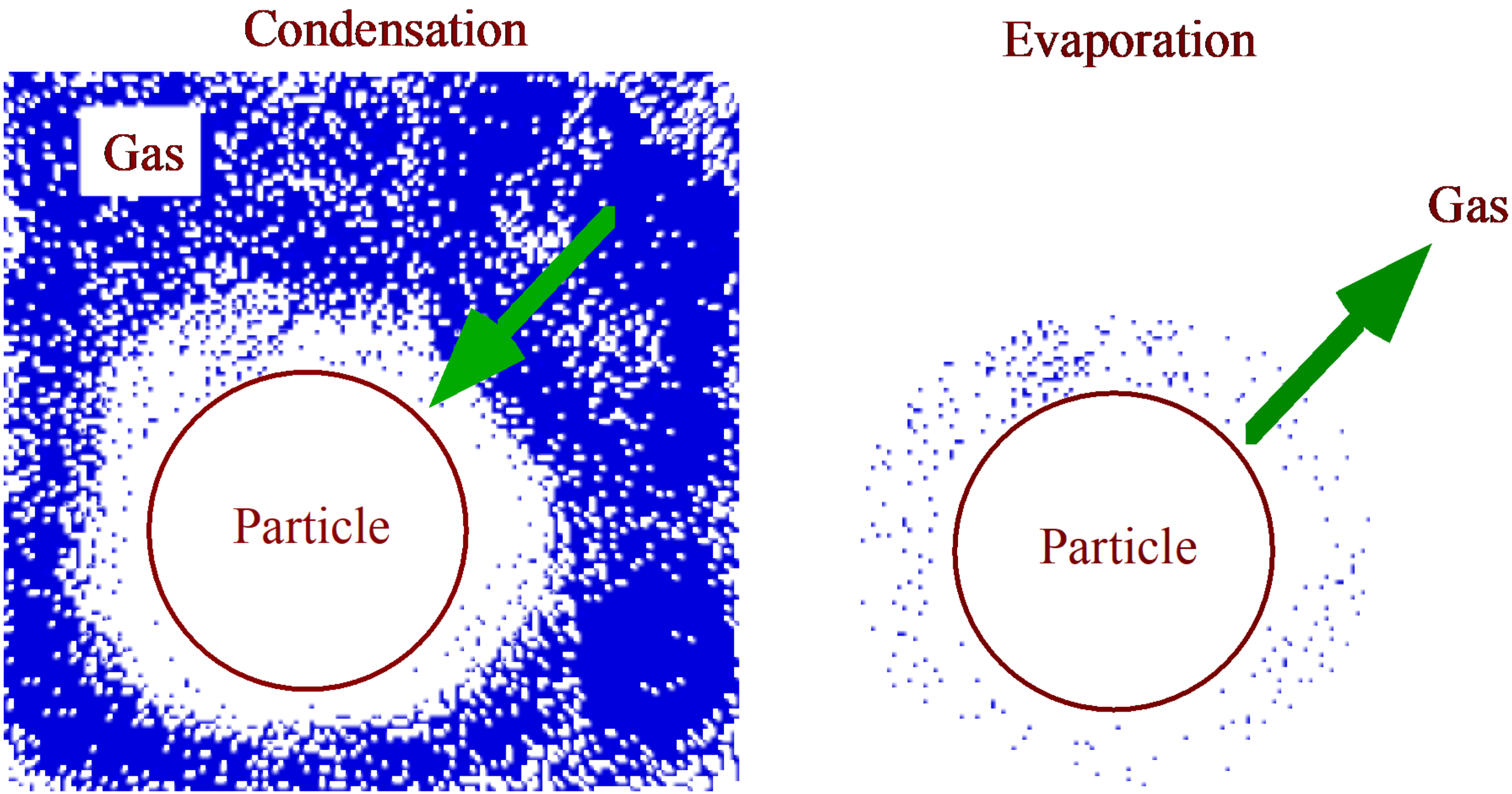


Figure 5.11

Condensing Gases

Condensation occurs primarily on accumulation mode since it contains the largest surface area concentration of all modes.

Water vapor

Condenses on accumulation and coarse-mode particles to form cloud drops

Sulfuric acid

Condensation onto accumulation mode affects visibility

High-molecular weight organic gases

Products of toluene, xylene, alkylbenzene, alkane, alkene, biogenic hydrocarbon oxidation condense onto accumulation mode primarily.

Condensation/Evaporation Equation

$$\frac{d\upsilon}{dt} = \frac{4\pi r D\left(p - p_s\right)}{\dfrac{D L_e \rho\, p_s}{\kappa T}\left(\dfrac{L_e m}{R^* T} - 1\right) + \dfrac{R^* T \rho}{m}}$$

Dissolution

Dissolution

Process by which a gas diffuses to and dissolves in a liquid on a particle surface.

Solvent

A liquid in which a gas dissolves

Solute

Gas, liquid, or solid that dissolves in a solvent

Solution

One or more solutes plus the solvent.

Common dissolving gases

$HCl(g)$, $HNO_3(g)$, $NH_3\ (g)$, $SO_2(g)$

Dissociation

Dissociation

Breakdown of dissolved molecules into ions.

Cations

Positively-charged ions (e.g., H^+, Na^+, K^+, Ca^{2+})

Anions

Negatively-charged ions (e.g., OH^-, Cl^-, NO_3^-, HSO_4^-, SO_4^{2-})

Electrolyte

Substance that undergoes partial or complete dissociation (e.g., NH_4NO_3, Na_2SO_4, HCl)

Dissolution/Dissociation

Addition of acid to solution increases [H^+], decreasing pH

Hydrochloric acid

$$HCl(g) \rightleftharpoons HCl(aq) \rightleftharpoons H^+ + Cl^-$$

Hydrochloric acid gas | Dissolved hydrochloric acid | Hydrogen ion | Chloride ion

Nitric acid

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

Nitric acid gas | Dissolved nitric acid | Hydrogen ion | Nitrate ion

(5.6) - (5.8)

Acidity

Measure of the concentration of hydrogen ions (H^+) in solution

$$pH = -\log_{10}[H^+] \qquad (5.4)$$

$[H^+]$ = molarity (M, moles of H^+ per liter of solution)

Higher $[H^+]$ --> lower pH --> more acidic solution

Acidity

In dilute water, the only source of H^+ is

$$H_2O(aq) \rightleftharpoons H^+ + OH^- \qquad (5.5)$$

Liquid water — Hydrogen ion — Hydroxide ion

$[H^+][OH^-] = 10^{-14}\ M^2$ --> $[H^+]=[OH^-]=10^{-7}\ M$

--> $pH = -\log_{10}[10^{-7}M] = 7$

Acid/Base

Acid

Substance that, when added to a solution, dissociates, increasing $[H^+]$, decreasing pH

Strong acid: Substance that dissociate readily (e.g., H_2SO_4, HCl, HNO_3)

Weak acid: Substance that dissociate less readily (e.g., H_2CO_3)

Base (alkali)

Substances that, when added to a solution, reduce $[H^+]$, increasing pH. (e.g., NH_3, $Ca(OH)_2$)

pH Scale

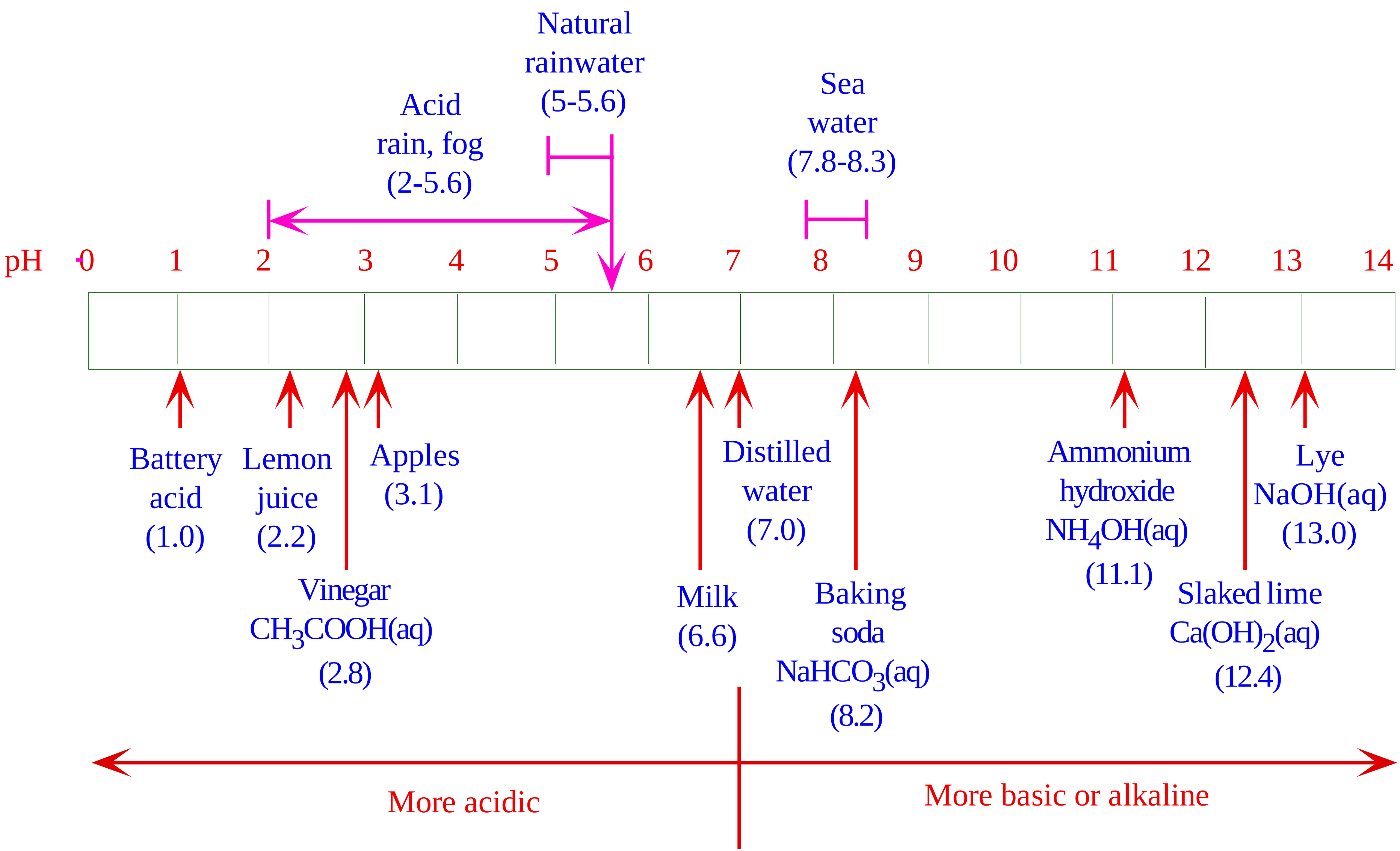


Figure 10.3

Sea-Spray Acidification

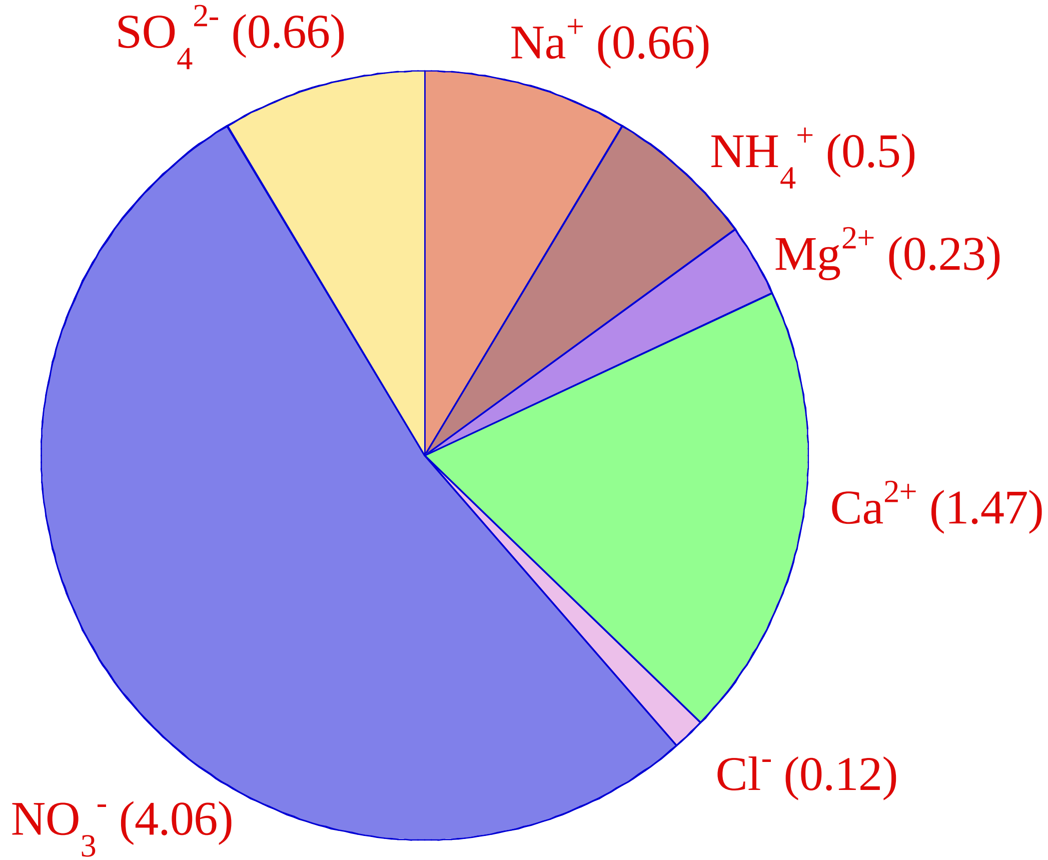


Figure 5.13
Particle composition (υg/m^3)
Riverside, CA

$$HNO_3(g) + Cl^- \rightleftharpoons HCl(g) + NO_3^- \quad (5.7)$$

Nitric acid gas	Chloride ion	Hydrochloric acid gas	Nitrate ion

Soil-Particle Acidification

Addition of acid to calcite-containing soil dust removes carbonate ion

$$CaCO_3(s) + 2HNO_3(g) \rightleftharpoons Ca^{2+} + 2NO_3^- + CO_2(g) + H_2O(aq)$$

Calcium carbonate	Nitric acid gas	Calcium ion	Nitrate ion	Carbon dioxide gas	Liquid water

(5.9)

Hydration

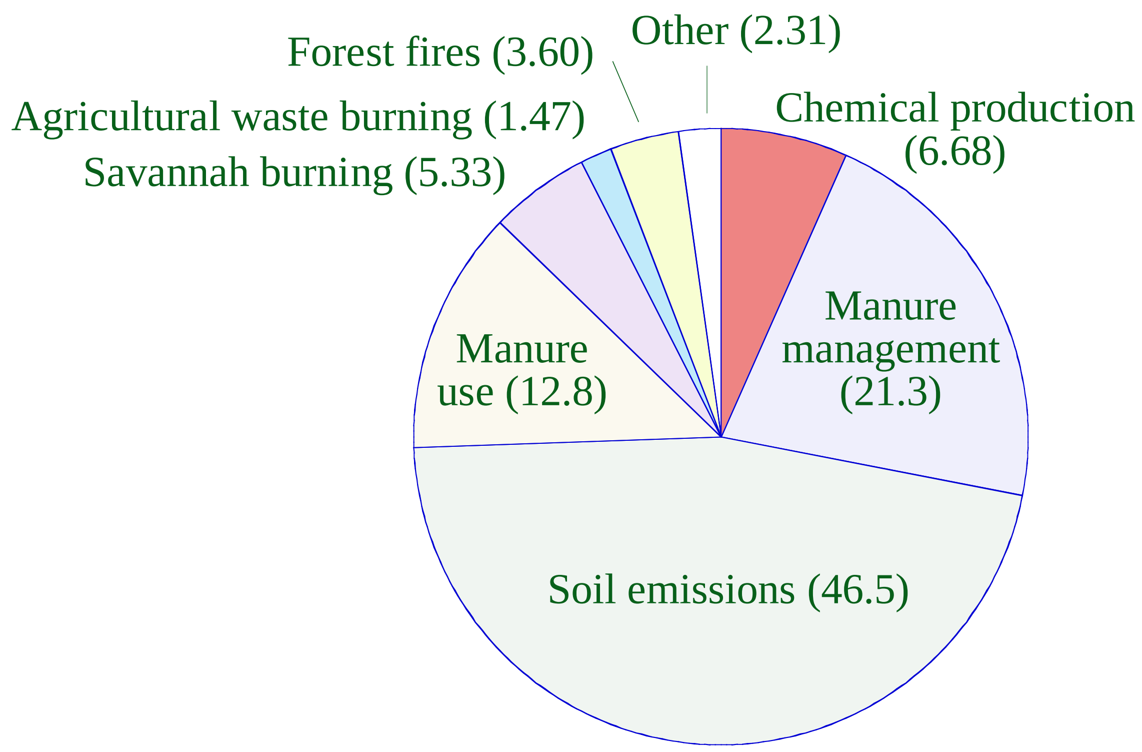
- Bonding of liquid water to solute (anions, cations, or undissociated molecules).
- The higher the relative humidity and greater the quantity of solute, the greater the liquid water uptake due to hydration.
- Hydration responsible for swelling of particles sufficiently to cause a haze when the relative humidity is below 100 percent.

Sulfuric Acid Condensation/Dissociation

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

Condensation occurs primarily on accumulation mode

Ammonia Dissolution/Dissociation



Percent worldwide ammonia emissions by source

$NH_3(g) \rightleftharpoons NH_3(aq)$

Ammonia gas — Dissolved ammonia

$NH_3(aq) + H^+ \rightleftharpoons NH_4^+$

Dissolved ammonia — Hydrogen ion — Ammonium ion

Solid Precipitation

When the relative humidity decreases, ions in solutions may combine (crystallize) to form solids (solid precipitation). Solids may also form by chemical reaction on the surface of particles.

Common solid formation reactions

$NH_4^+ + NO_3^- <=> NH_4NO_3(s)$ ammonium nitrate

$2NH_4^+ + SO_4^{2-} <=> (NH_4)_2SO_4(s)$ ammonium sulfate

$Ca^{2+} + SO_4^{2-} + 2H_2O(aq) <=> CaSO_4\text{-}2H_2O(s)$ gypsum

Particle Health Effects

Hazardous compounds in particles

Benzene, PAHs, metals, sulfur compounds

Metals

Lung injury, bronchio constriction, increased infection

PM_{10}

Asthma, chronic obstructive pulmonary disease, increased mortality, higher hospitalization and health-care visits for respiratory and cardiovascular disease. May be no low threshold for health-related problems due to PM_{10}.

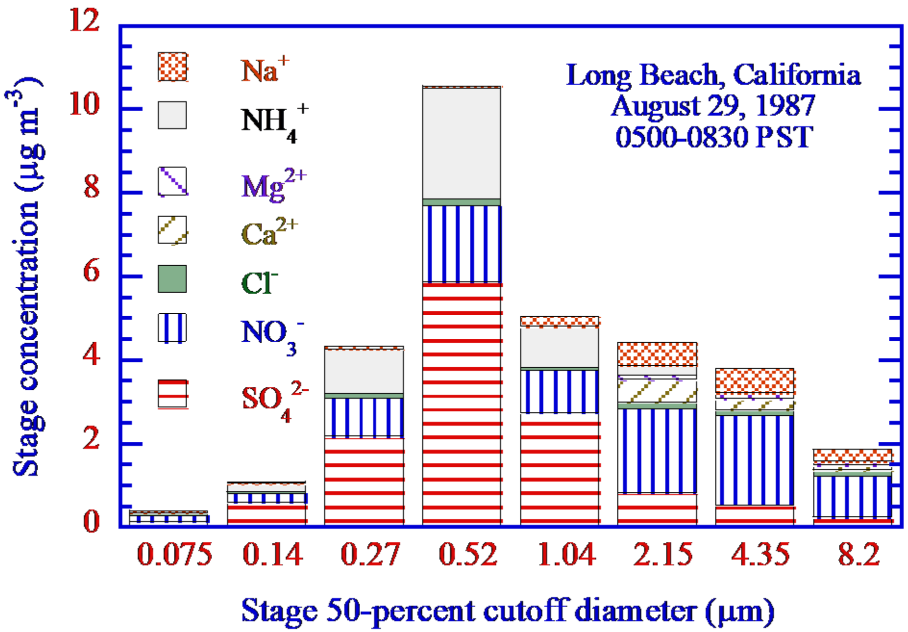
$PM_{2.5}$

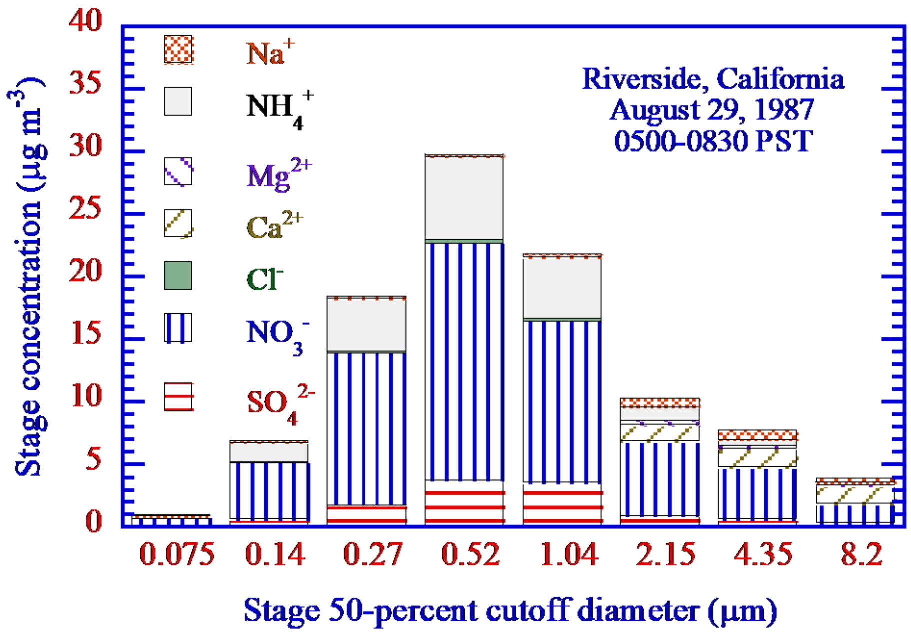
More respiratory illness and premature death than larger particles. Long-term city exposure may reduce life by two years.

Total air pollution mortality (due mostly due to particles)

2.5-3 million deaths/yr worldwide from air pollution; 1.6 million in due to indoor burning of biomass, coal.

Aerosol Particle Composition vs. Size





Particle Mixing State

- **External mixture**

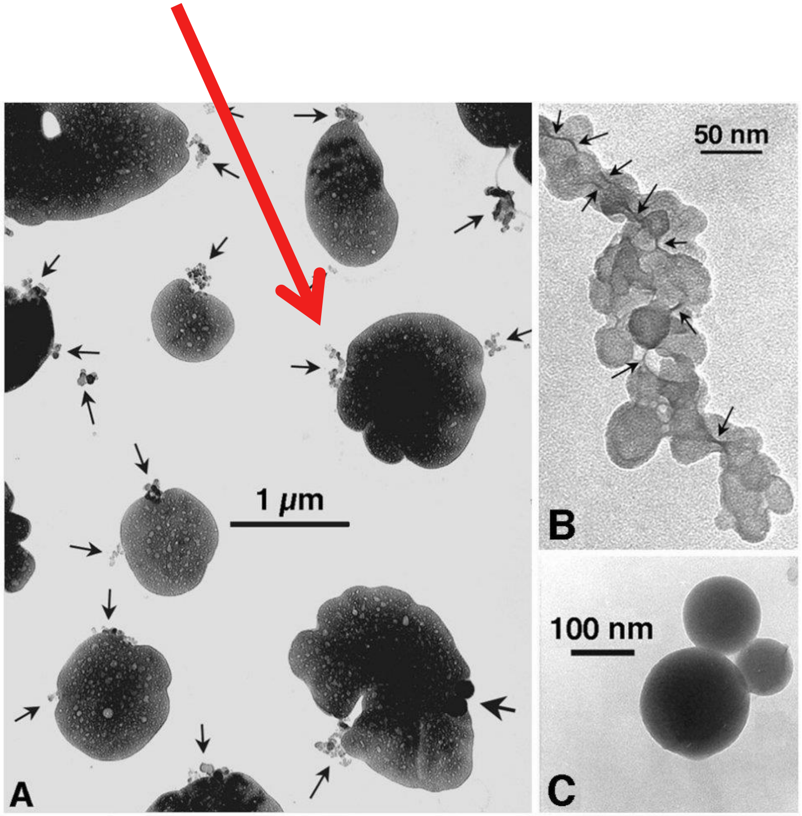
  Particle composition is the same as that when the particle was emitted.

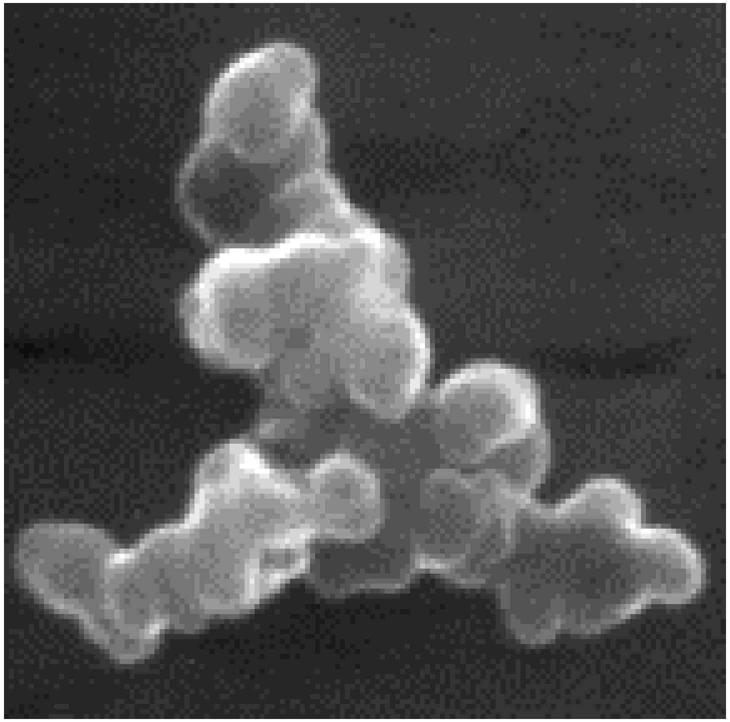
- **Internal mixture**

  Particle composition differs from that when it was emitted due to condensation, dissolution, coagulation, and other physical processes affecting composition.

Internally- and Externally-Mixed Soot Particles

Soot inclusion

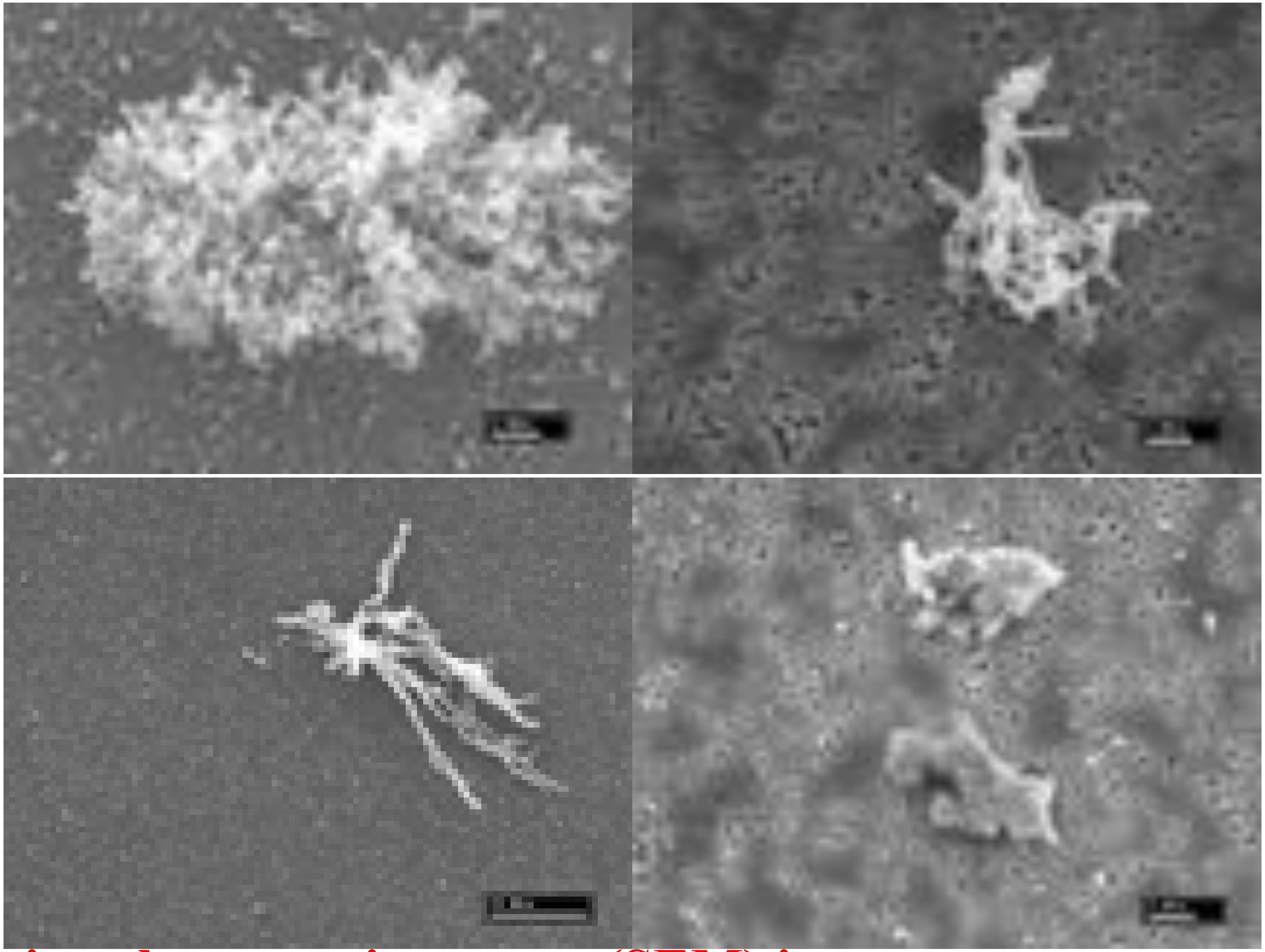




Pósfai et al. (1999)

Strawa et al. (1999)

Ash, Combusted Plant Fiber, Elongated Ash, Soil Dust



Scanning electron microscopy (SEM) images

Reid and Hobbs (1998)

Lungs of Teenage non-smoking Teenager in Los Angeles, 1970s

台灣風險分析學會

Taiwan Chapter of Society for Risk Analysis

Global Perspectives of Risks

2015 年第 2 期: WHO 最新的報告指出，空污造成歐洲國家居民死亡與疾病的經濟負荷為每年 1.6 兆美元

Release: May 4, 2015

許惠悰
中國醫藥大學健康風險管理系