

CE 435: Environmental Pollution Management

**January 2018 Semester
Level-4, Term II**

CN-2

**Department of Civil Engineering
Bangladesh University of Engineering and Technology
(BUET)**

Air Pollution

Formation, Sources and Effects of Criteria Pollutants

(A) Particulate/Particulate Matter (PM)/ Aerosol

Consists of any dispersed matter in the air, solid or liquid (except pure water), with size ranging from molecular clusters of 0.005 μm to coarse particles of up to 100 μm .

Particulate/Particulate Matter (PM)/ Aerosol

Terms Used to Describe PM:

- **Dust:** solid particles are called dust if they are caused by grinding and crushing operations.
- **Fumes:** solid particles are called fumes if they are formed when vapors condenses.
- **Mist, Fog:** liquid particulates.
- **Smoke, Soot, Black Carbon (BC):** composed primarily of carbon that results from incomplete combustion.
- **Smog:** derived from smoke and fog (not to be confused with “photochemical smog”).

Particulate Matter (PM):

Black Carbon (BC)/ Soot:

Black Carbon (BC)/ Soot:

The BC or soot consist mostly of solid particles made up of vast numbers of carbon particles fused together in benzene rings.

Major sources of BC include:

- **Transportation sector** (diesel vehicles, flexible pavement construction); BC typically constitutes ~75% of PM emitted from older diesel engines.
- **Residential cooking** (traditional stove/ fuel) and heating,
- **Industrial sector** (brick kilns), and
- **Agricultural burning.**

Particulate Matter (PM):

Black Carbon (BC)/ Soot:

Health effects:

While BC themselves can irritate lung, most often it is the larger organic molecules that stick to the surface of BC [mostly Polycyclic/Polynuclear Aromatic Hydrocarbons (PAHs), e.g., benzo-a-pyrene, a human carcinogen] that are responsible for most serious health effects. PAHs are formed when C-containing hydrocarbons are not completely oxidized during combustion.

Particulate Matter (PM):

Black Carbon (BC)/ Soot:

Climate effects:

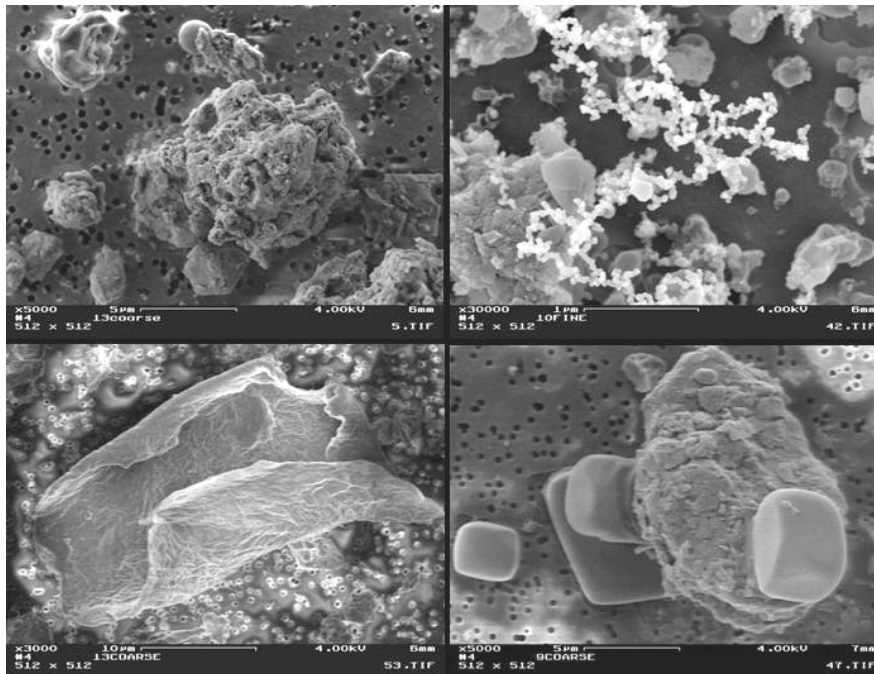
BC causes warming of atmosphere by a number of processes:

- When deposited on ice/snow, BC reduces albedo of these surfaces, increasing both atmospheric warming and melting rate caused by increased absorption of heat by the darker snow/ice around the world. This affects the water cycle and increases the risks of flooding.
- Black carbon aerosols have a large impact on regional circulation and rainfall patterns (e.g., monsoon) as they cause significant asymmetry in heating patterns over a region;

Particulate Matter (PM):

Size of PM: Aerodynamic Diameter

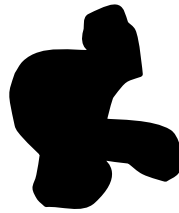
Although particles may have irregular shapes, their size can be described by an equivalent “**aerodynamic diameter**” determined by comparing them with perfect spheres having the same settling velocity.



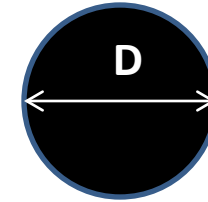
Particulate Matter (PM):

Size of PM: Aerodynamic Diameter

∴ Aerodynamic diameter of this particle = D



↓
Settling velocity
= 15 cm/min



↓
Settling velocity
= 15 cm/min

Thus, aerodynamic diameter of a “particle (PM)” is equal to the diameter of a “perfect sphere”, whose settling velocity is equal to the settling velocity of the “particle (PM)”.

Stokes law can be used to estimate settling velocity (e.g., a 10- μm particle has a settling velocity of approximately 20 cm/min). **PM_{2.5}** means PM with aerodynamic diameter $\leq 2.5 \mu\text{m}$.

Particles of most interest have aerodynamic diameter in the range 0.1 to 10 μm . Particles smaller than these undergo random (Brownian) motion and through coagulation generally grow to sizes $> 0.1 \mu\text{m}$. Particle larger than 10 μm settle quickly.

Particulate Matter (PM):

Distribution and Characteristics

- **About 90% of all respirable PM in the Earth's atmosphere are natural; about 10% are anthropogenic.**
- **However, most natural PM are relatively harmless (e.g., soil, sea-spray, biological materials). PM of anthropogenic origin, on the other hand, are often toxic.**
- **PM of anthropogenic origin are considered more harmful because of their:**
 - (a) non-uniform distribution;**
 - (b) chemical composition; and**
 - (c) size distribution (smaller)**

Particulate Matter (PM):

Distribution and Characteristics (contd.)

(1) Non-uniform Distribution: Anthropogenic PM are concentrated in cities and industrial areas.

(2) Chemical Composition: About 40 elements could be found in PM. Most important elements include:

Al, Fe, Na, Si ----- Mostly from natural (soil) origin
(Typical Soil: 8% Al, 6% Fe)

C, S, Pb, V, Ni, As, Ag, Cu, Cd ----- Mostly from anthropogenic sources (mainly combustion of fuel); often harmful organic contaminants, e.g., PHAs are found to be associated with BC/Soot

Particulate Matter (PM):

Distribution and Characteristics (contd.)

(3) Size Distribution: PM of anthropogenic origin (e.g., PM in automobile exhaust) are smaller size; while those of natural origin (e.g., soil dust) are usually relatively larger.

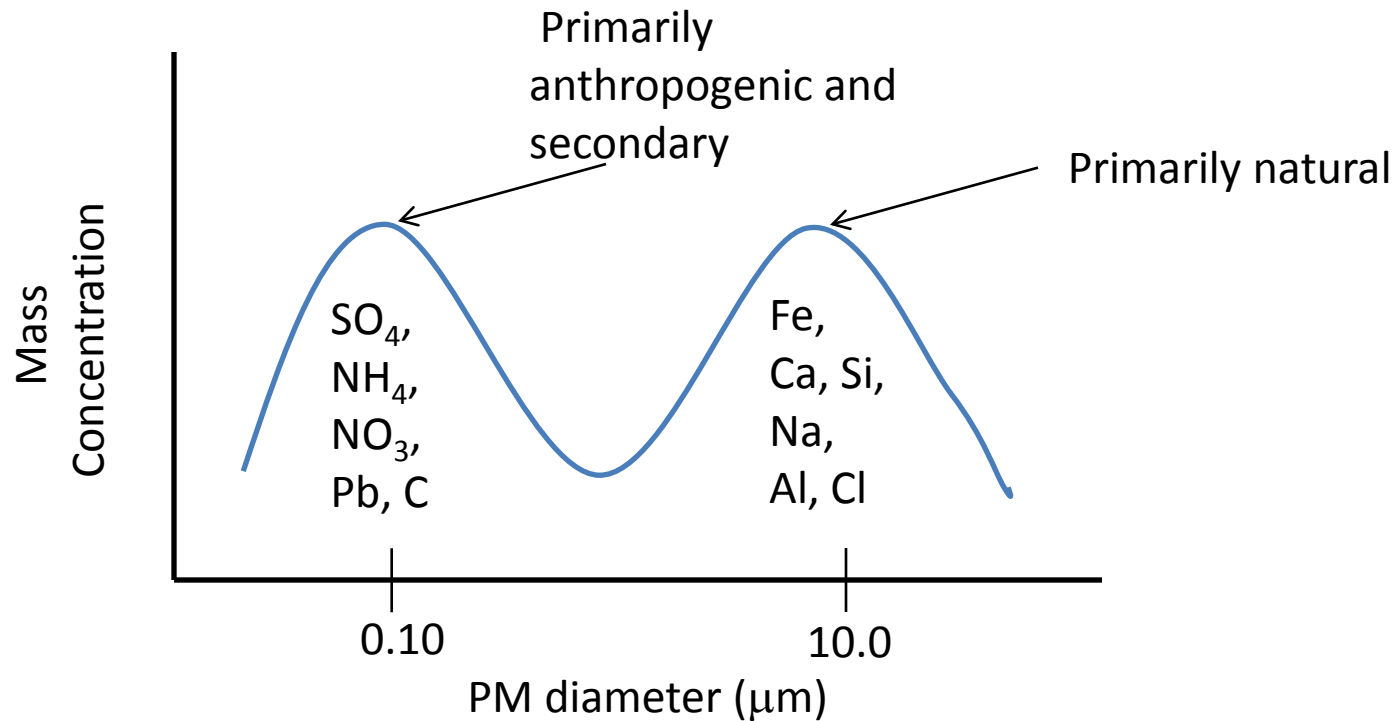


Fig.: Idealized aerosol mass distribution showing typical segmentation of chemical species into fine and coarse fractions

Source Apportionment PM in Dhaka

(Guttikunda, 2009)

Major sources of PM in Bangladesh include:

- Brick kilns
- Vehicular emission
- Road dust
- Soil dust
- Rice Parboiling Unit
- Certain industries (steel mill, cement factories)

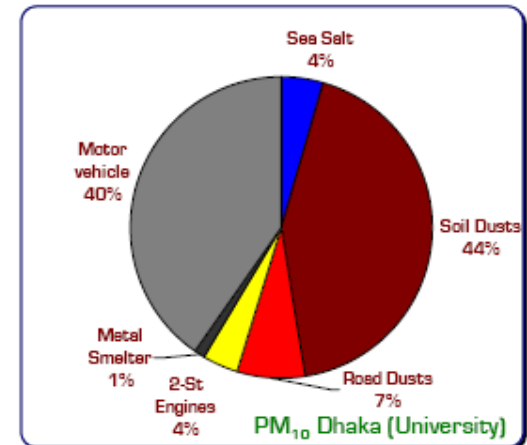
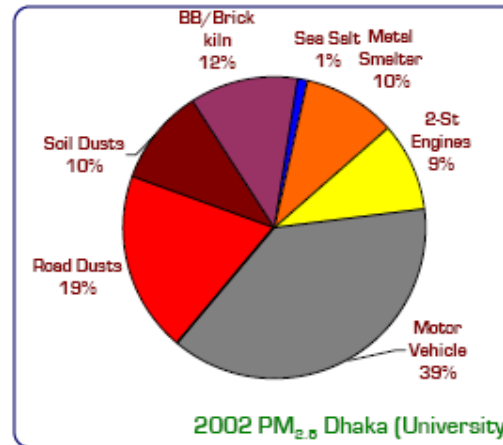
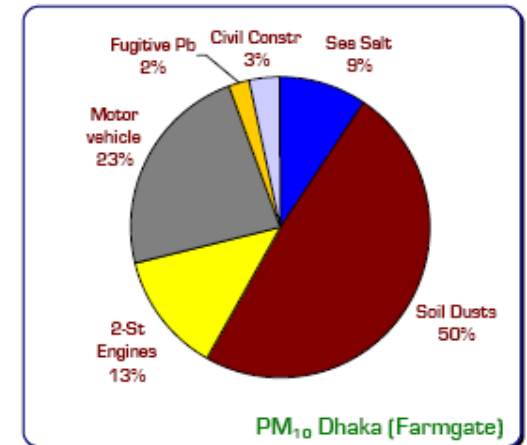
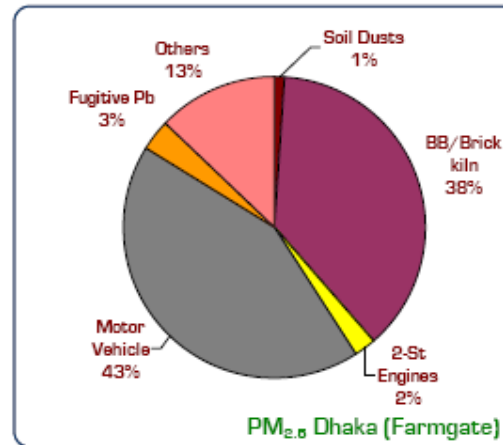


Figure 3: Source apportionment results for Dhaka

Source Apportionment of PM in Rajshahi

(Guttikunda, 2009)

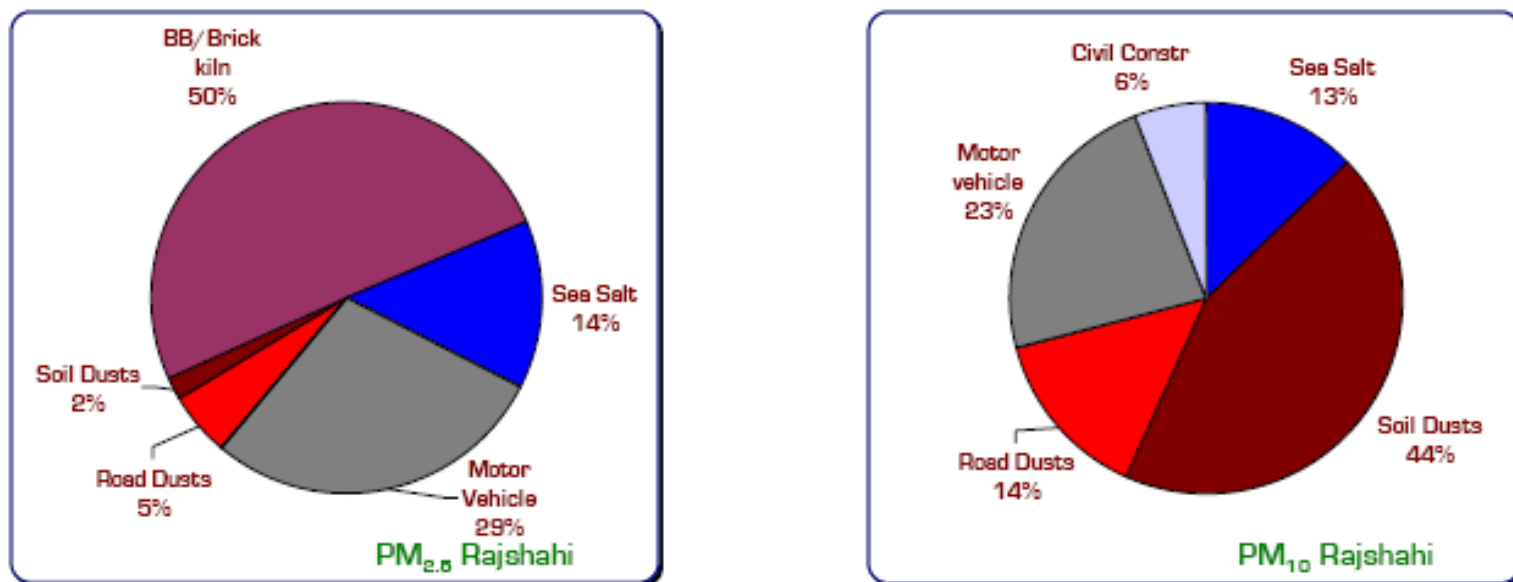
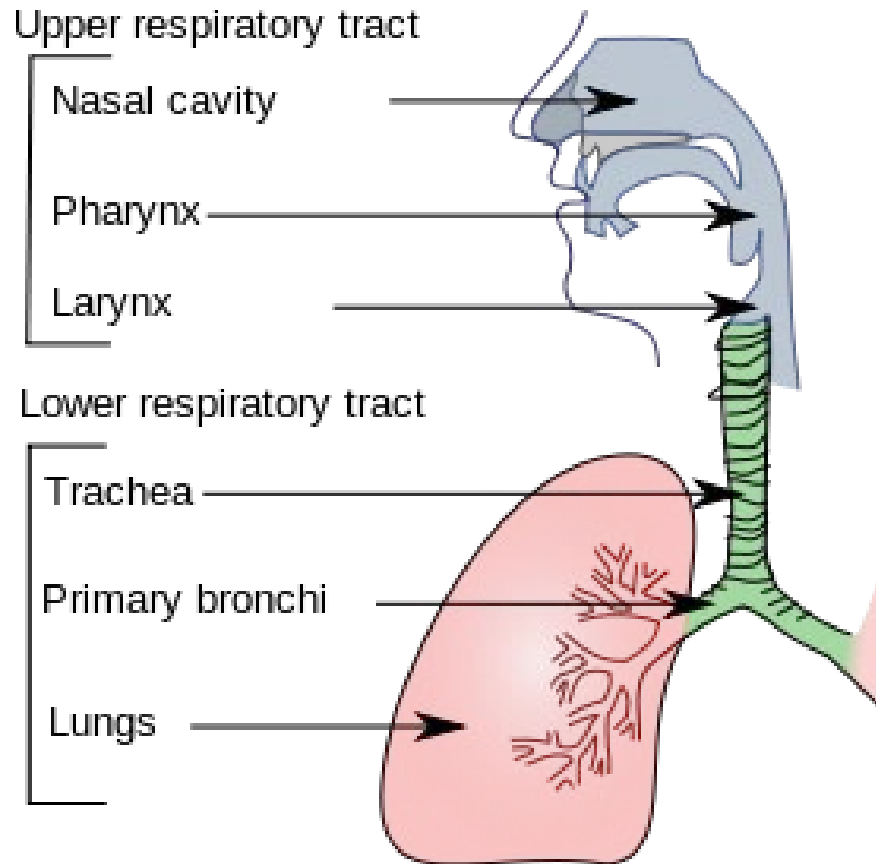


Figure 4: Source apportionment results for Rajshahi

Health Effects of PM

- **PM suspended in the air enter our body when we breath. These particles include:**
 - (a) **Natural particles (e.g., bacteria, viruses, pollen, sea salt)**
 - (b) **Anthropogenic emissions (e.g., cigarette smoke, vehicle exhaust)**
- **The hazard posed by these particles depends on their “chemical composition” as well as “where they deposit” within the respiratory system.**
- **Hence, we need to learn a few things about our respiratory system.**

Deposition of PM in the Respiratory System



Human Respiratory System

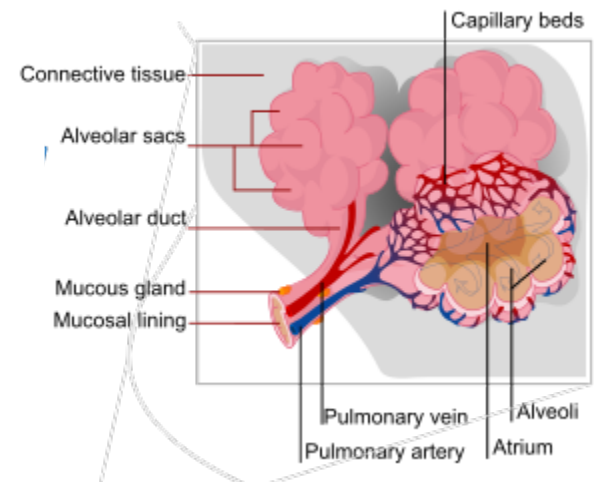
Deposition of PM in the Respiratory System

From the viewpoint of respiratory deposition PM, the respiratory system can be divided into 3 regions:

(1) Head Airways Region: Nasal airway and Oral airway

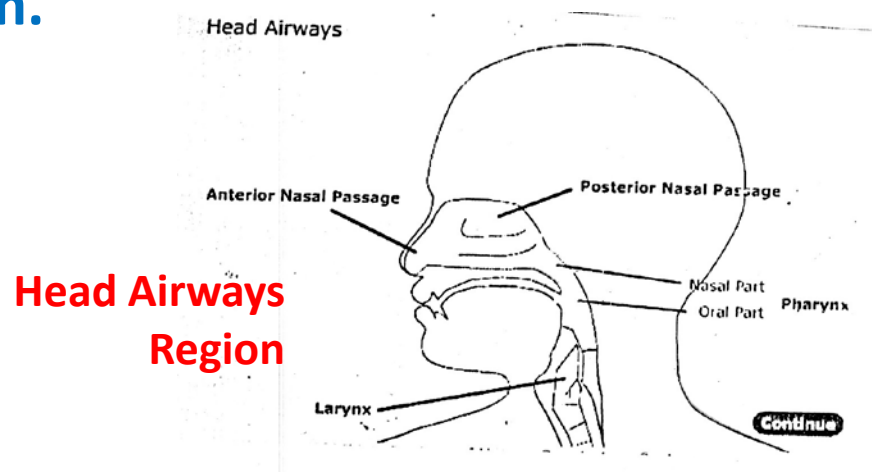
(2) Lung Airways Region (Tracheo-bronchial Region):
From “trachea” to “terminal bronchioles”
(23 airway branching)

(3) Pulmonary Region (Alveolar Region):
Across the alveolar membrane O_2 and CO_2 counter-diffuse
Surface area $\sim 75 \text{ m}^2$



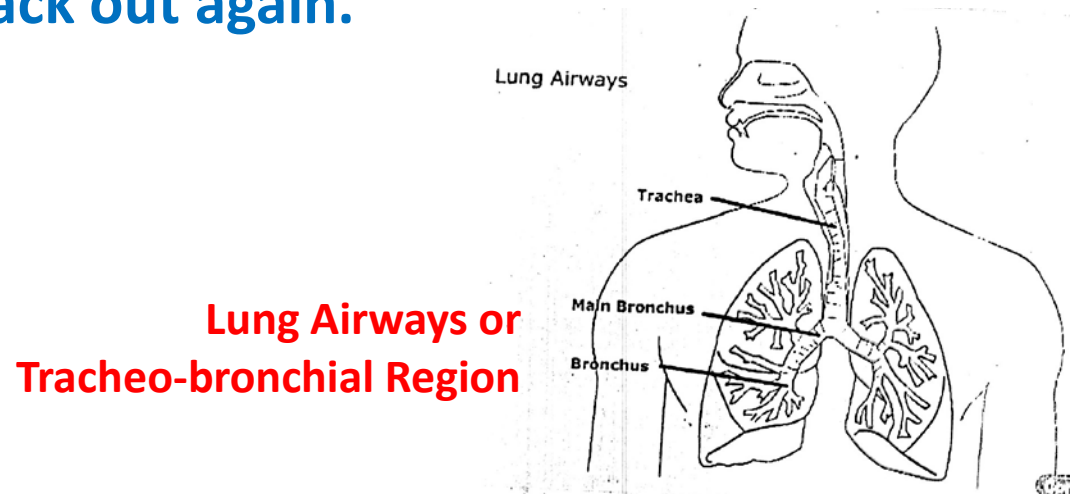
Deposition of PM in the Respiratory System

- Large PM entering the respiratory system can be trapped by hairs and linings of the nose. Once captured, they can be driven out by cough and sneeze.
- The “nasal path” is usually more efficient at removing PM than the “oral path”. Deposition of particles in the head region during inhalation is essentially total for particles with diameter $> 10 \mu\text{m}$. During mouth breathing, the corresponding size is $15 \mu\text{m}$.



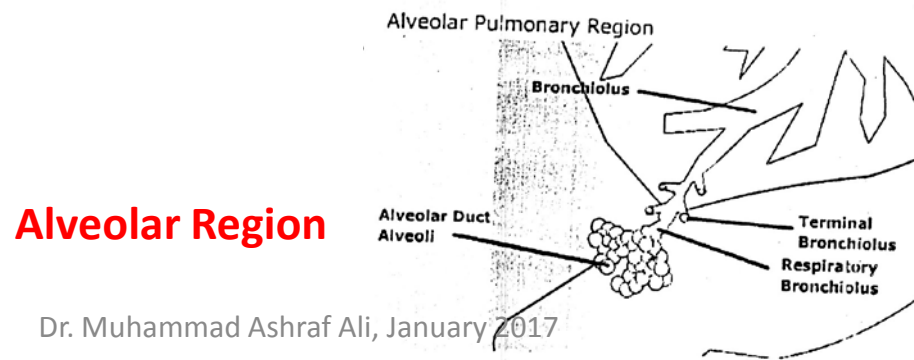
Deposition of PM in the Respiratory System

- Smaller particles that make it into the tracheo-bronchial system (i.e., lung airways) can be captured by mucus, worked back to throat by the tiny hair-like cilia, and removed by swallowing or spitting (muco-ciliary mechanism).
- Smaller PM are often able to traverse deeper, but depending on size they may or may not be deposited there. Some PM are so small that they tend to follow the airstream into the lung and then right back out again.



Deposition of PM in the Respiratory System

- Alveolar region does not have the muco-ciliary mechanism (because it is designed for gas exchange). It takes months/years to clear insoluble PM deposited here. **Fibrogenic dusts, such as silica, asbestos and coal dust, interfere with cleaning mechanism resulting in “fibrosis” of the region. Insoluble radioactive materials deposited in this region may cause significant damage due to long retention time.**
- Soluble materials can pass through alveolar membrane and be transported to other parts of body. Hence, it is the region where viruses invade and also the region for therapeutic aerosol delivery.



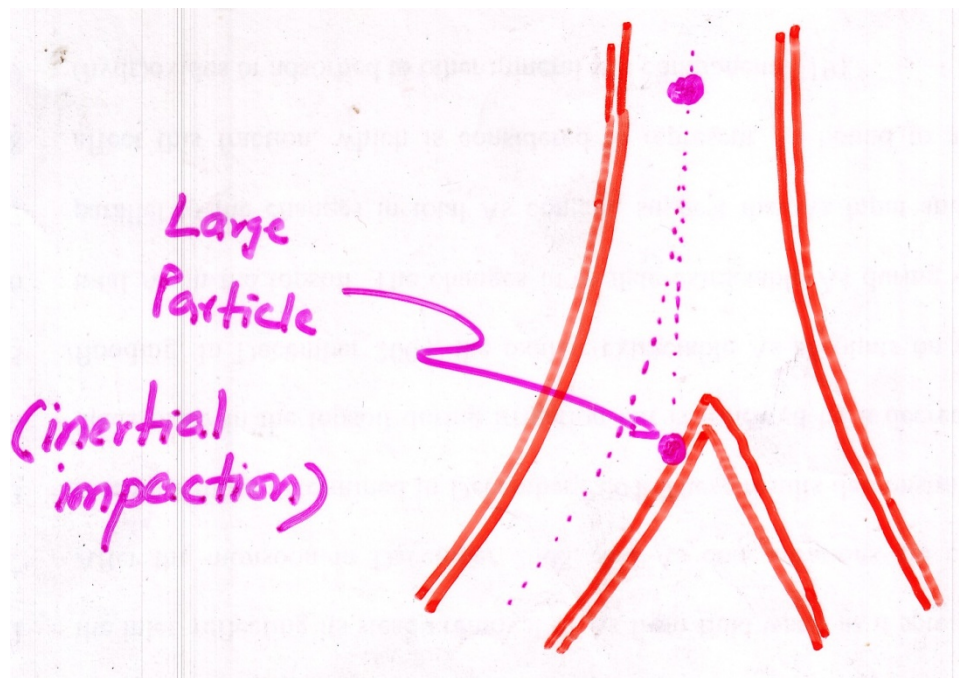
PM Deposition Mechanism in Respiratory System

Most important mechanisms are:

- (1) Impaction**
- (2) Settling**
- (3) Diffusion/ Brownian motion**
- (4) Interception**

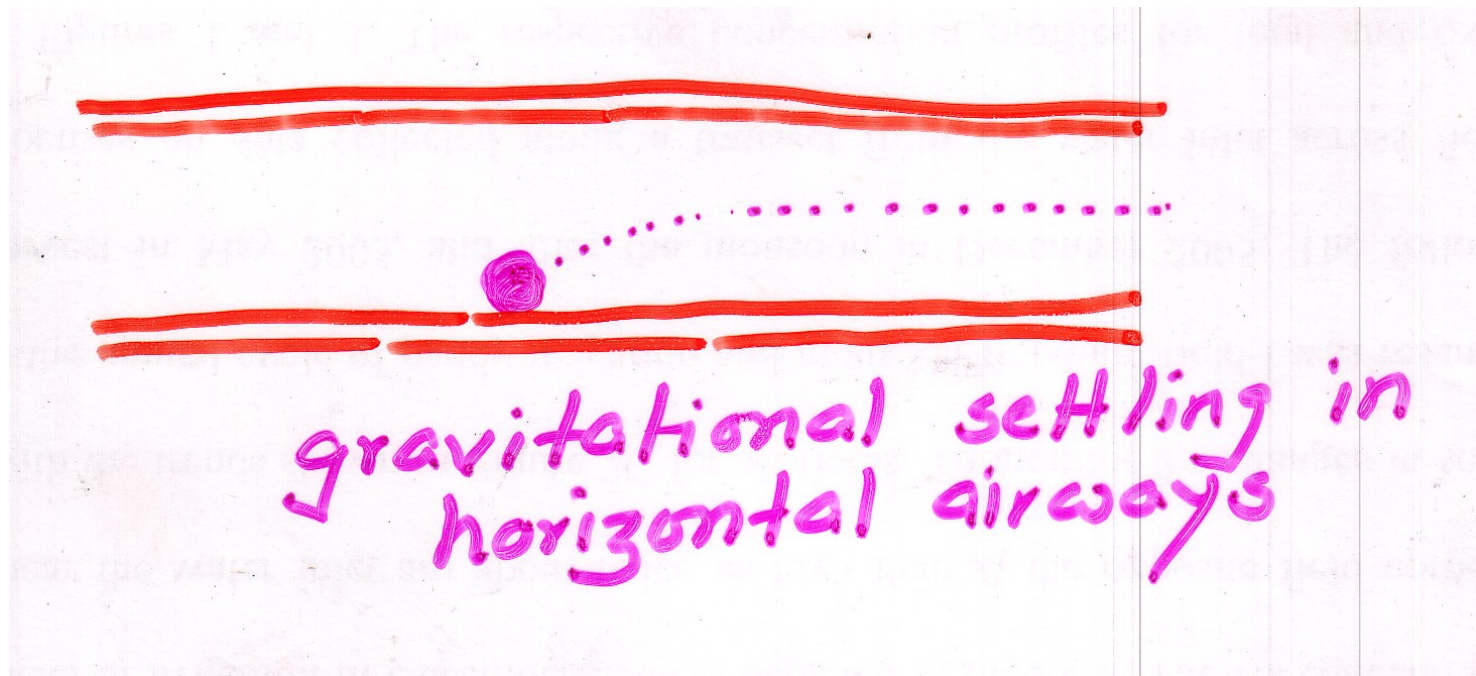
(1) Impaction

Collection by impaction is due to a particle's inertia that makes the particle deviate from the air stream when the air stream makes a turn. Impaction is important when the particle size or the velocity is large in a curved pathway. Hence, it is the primary mechanism in bronchial region



(2) Settling

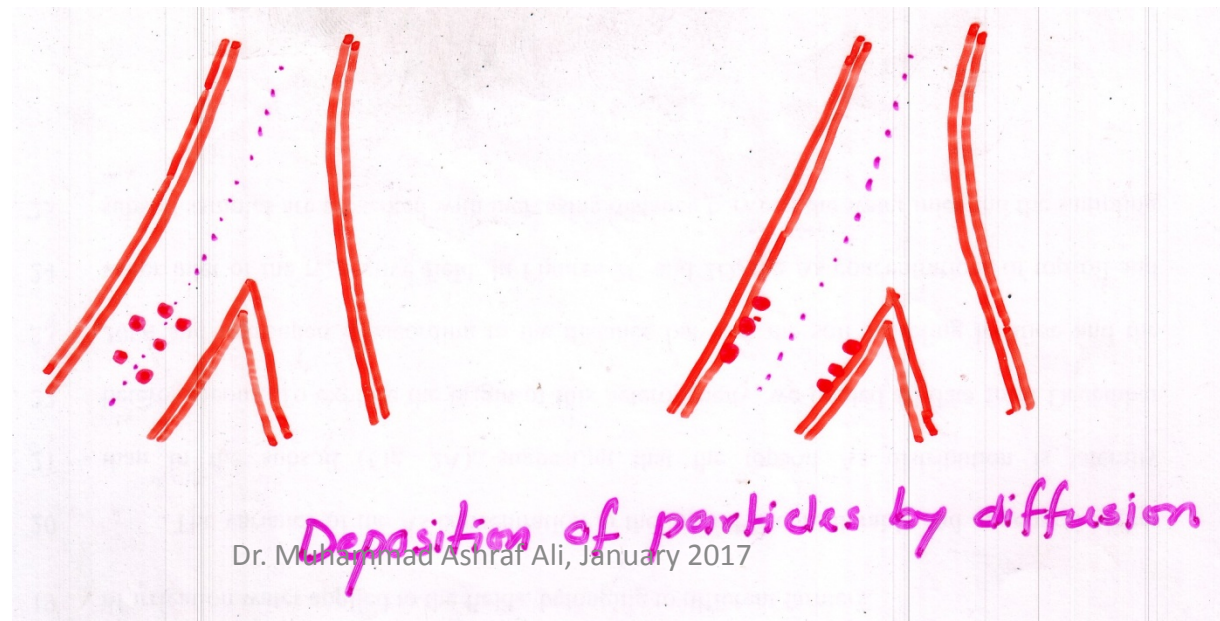
When flow velocity is small and the airway dimension is small, settling then becomes an important role for large particles. It's especially effective in horizontally oriented airways.



(3) Diffusion/ Brownian Motion

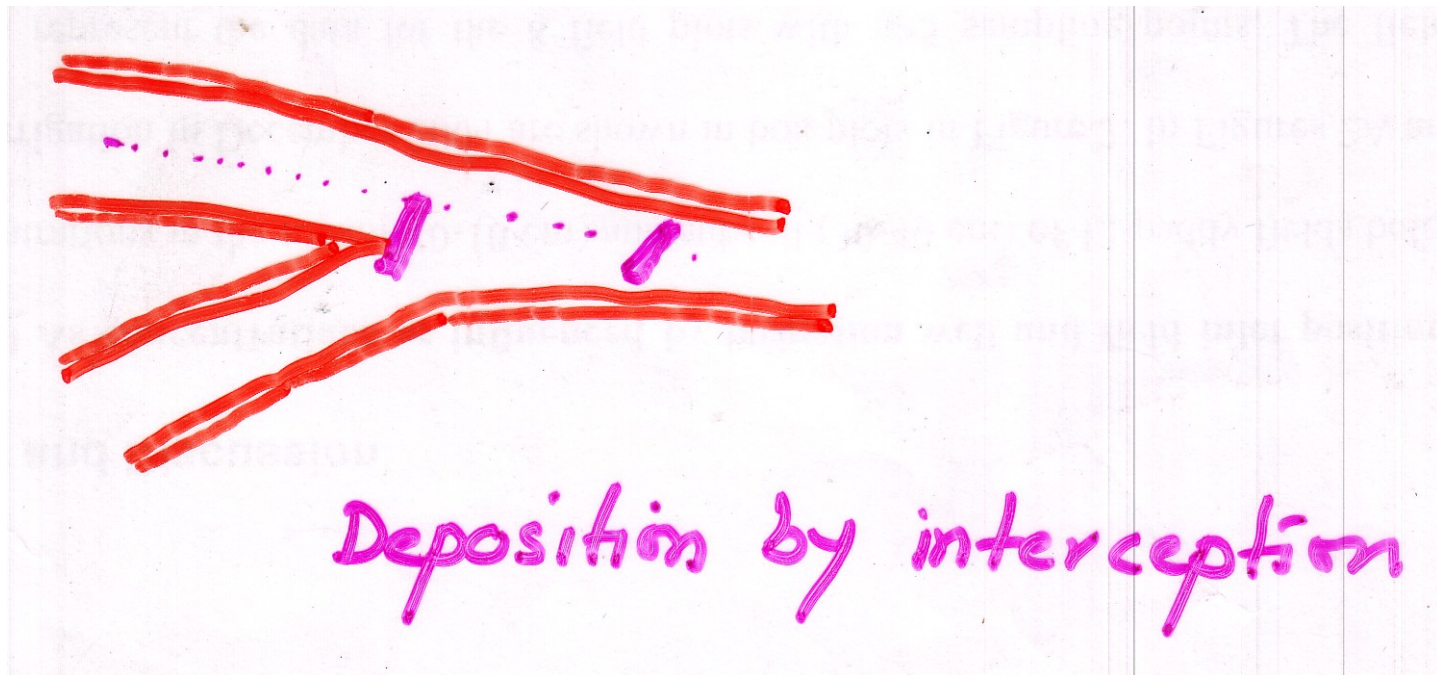
In small airway, where distance is short and residence time is long, diffusion is an important mechanism for small particles ($< 0.5 \mu\text{m}$). Brownian motion is the microscopic random motion of small particles due to random collisions by gas molecules.

Macroscopically, we see overall movement of particles from a high concentration region (in this case, center of air stream) to a lower concentration region (in this case, airway wall). Effectiveness of this mechanism increases as particle size decreases.



(4) Interception

When a particle follows the air stream without deviation, it can still contact the airway surface because of its physical size. This mechanism is called interception. Usually interception is not critically important in our respiratory system except for long fibers that are long in one dimension.



Health Effects of PM

- Particulates (both PM₁₀ and PM_{2.5}) are the most serious air pollutants in urban/industrial areas (including Dhaka). Adverse health outcomes have been found to be strongly correlated with PM (especially PM_{2.5}) concentrations.
- Extent of health effects depends on size, composition and concentration of PM, length of exposure, and where they deposit in the respiratory system.
- Exposure to PM (especially PM_{2.5} and BC) is associated with increased incidences of respiratory illness, chronic bronchitis, broncho-constriction, decrement of pulmonary function, and increased mortality rates.
- Adverse effects associated with short-term exposure to PM include increases in the rate of asthma attacks.

(B) Lead

- Most lead emissions come from vehicles burning gasoline containing the antiknock additive, tetraethyl lead $(C_2H_5)_4Pb$.
- **Lead is emitted to the atmosphere primarily in the form of inorganic particulates.**
- Human exposure to airborne lead primarily result from inhalation. It can also be ingested after lead has deposited onto foodstuff.
- **About $\frac{1}{3}$ of lead particles inhaled are deposited in the respiratory system, about $\frac{1}{2}$ of those are absorbed by bloodstream.**
- Adverse impact of lead poisoning include aggressive, hostile and destructive behavioral changes; learning disabilities; seizures; severe and permanent brain damage; and even death.
- **Vulnerable groups include children and pregnant women.**

(B) Lead (contd.)

- **Pb was identified as a major health hazard in Bangladesh in early as 1980s; average blood Pb concentration of 55 ± 18 $\mu\text{g}/\text{dL}$ was observed in a group of 100 adults in Dhaka.**
- **In early 1990s, tests confirmed presence of Pb in ambient air in Dhaka, and petrol additives were identified as a major source. Subsequent advocacy by various groups led to total phase out of Pb from petrol in Bangladesh by mid 1999, which had reduced Pb concentration in ambient air significantly.**
- **Apart from Pb in road dust, other potential sources of Pb in Bangladesh can be paint, fabric and leather dyeing (hence textile and leather industries), metal smelters and battery industries.**

(B) Lead (contd.)

Ambient Lead Concentration in Dhaka

Year	Study 1 Pb in PM _{2.5} ($\mu\text{g}/\text{m}^3$)	Study 2 Pb in PM _{2.5} ($\mu\text{g}/\text{m}^3$)	Study 2 Pb in PM ₁₀ ($\mu\text{g}/\text{m}^3$)	Ratio of Pb in PM ₁₀ to Pb in PM _{2.5}
1994		0.312±0.485	0.522±0.614	1.67
1997	0.265±0.549	0.256±0.532	0.461±0.775	1.80
1998	0.370±0.644	0.370±0.636	0.507±0.669	1.37
1999	0.225±0.370	0.225±0.370	0.342±0.420	1.52
2000	0.106±0.179	0.106±0.179	0.160±0.192	1.51
2001	0.130±0.163			(average 1.57)
2002	0.227±0.784			
2003	0.166±0.467			
2004	0.198±0.611			
2005	0.102±0.207			
Reference	Begum & Biswas	Biswas et al. 2003	Biswas et al. 2003	

Air quality standard for Lead: 0.5 $\mu\text{g}/\text{m}^3$ (annual average)

Dr. Muhammad Ashraf Ali, January 2017

(B) Lead (contd.)

Blood lead Concentration in Bangladesh

Study year	Location	Blood Pb ($\mu\text{g}/\text{dL}$)*	Sample size	Reference
1980	Dhaka	55±18	100 adults	Khan et al. 1980
2000	Dhaka	15 (90% of sample > 10)	779 children (4-12 yr)	Kaiser et al. 2001
2007-2008	Dhaka-residential	2.5±3.3 (5% > 10)	57 children (6-12 yr)	Mitra et al. 2009
2007-2008	Dhaka-industrial	24.6±10.3 (99% > 10)	105 children (6-12 yr)	Mitra et al. 2009
2007-2008	Dinajpur	7.2±6.3 (14% > 10)	183 children (6-12 yr)	Mitra et al. 2009

10 $\mu\text{g}/\text{dL}$ often considered a safe level

- It is clear that Pb pollution in industrial areas is higher than other areas. Thus, efforts should continue to identify hotspots of Pb pollution, and take necessary measures to reduce emissions.

(C) Carbon Monoxide (CO)

Formation of CO:

(1) Incomplete combustion of Carbon/ Carbon containing fuel:



Incomplete combustion results when any of the following 4 variables are not kept sufficiently high: (i) Oxygen supply; (ii) Combustion temperature; (iii) Gas residence time at high temp.; and (iv) Combustion chamber turbulence.

(2) Industrial production of CO: by high temperature reaction between CO₂ and Carbon containing material.



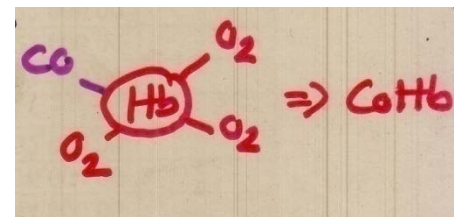
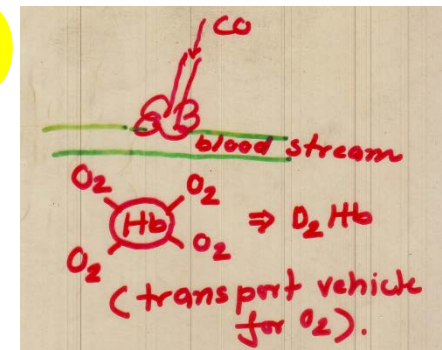
(C) Carbon Monoxide (CO) (contd.)

Sources of CO:

- **Transportation (most significant, often accounts of most of the CO emission in urban areas)**
- **Industrial processes**
- **Miscellaneous burning**
- **Natural (e.g., volcanic activity)**

(C) Health Effects of Carbon Monoxide (CO)

- The effects of CO exposure are reflected in the O₂ carrying capacity of blood.
- In normal functioning, hemoglobin (Hb) molecules carry O₂ which is exchanged for CO₂ in the capillaries connecting arteries and veins.
- CO diffuses through the alveolar wall and competes with O₂ for one of the 4 iron sites in Hb molecule. Affinity of the iron site for CO is about 210 times greater than for O₂.
- When a Hb molecule acquires a CO, it is called “Carboxy-hemoglobin”



Carboxy-hemoglobin
(COHb)

(C) Health Effects of Carbon Monoxide (CO) (contd.)

Formation of COHb causes two problems, resulting in O₂ starvation:

- (1) Less sites available for CO**
 - (2) Greater amount of energy binding the three O₂ molecules to Hb, so that they cannot be released easily (to be exchanged for CO₂)**
- Formation of COHb is a reversible process, with half life for dissociation after exposure of about 2 to 4 hours for low concentrations.**

(C) Health Effects of Carbon Monoxide (CO) (contd.)

When bloodstream carries less O₂, brain functions is affected and heart rate increases in an attempt to offset O₂ deficit.

Sensitive Group: Elderly, fetus, individuals with heart disease.

The health effects of CO exposure are summarized in Fig. (see book for details).

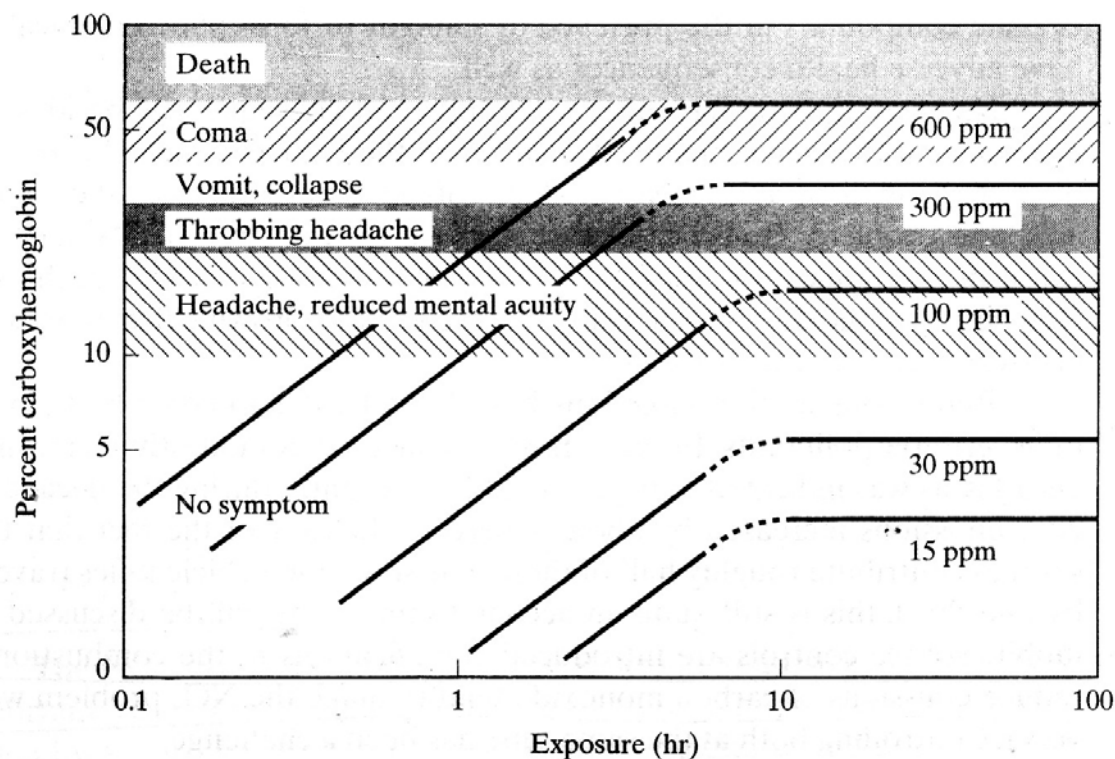


FIGURE 7.6 Effects of exposure to carbon monoxide. (Source: Seinfeld, 1986)

(C) Health Effects of Carbon Monoxide (CO) (contd.)

Estimation of %COHb in Blood:

The amount of COHb in blood is related to CO concentration and exposure time; often related by empirical equations, e.g.,

$$\%COHb = \beta(1 - e^{-\gamma t}) (CO)$$

Where,

%COHb = COHb as a percent of saturation

(CO) = CO concentration in ppm

$\gamma = 0.402 \text{ hr}^{-1}$; $\beta = 0.15\%$ per ppm CO

t = exposure time in hours

(C) Health Effects of Carbon Monoxide (CO) (contd.)

- CO in busy roadways often range from 5 to 50 ppm (1-hr standard 35 ppm);
- CO is an important indoor air pollutant;
- Cigarette smoke contains CO ~20,000 ppm, which is diluted to 400 – 500 ppm during inhalation; cigarette smoking often raises CO in restaurants to 20 – 30 ppm (close to 1-hr standard);
- 24-hr avg. indoor CO concentration due to wood/charcoal combustion can be 100 to 200 ppm, with peak of 400 ppm lasting for several hours.
- People who are consistently exposed to high levels of CO, like heavy smokers or women in rural kitchen, often adjust to compensate for lower levels of oxygen in bloodstream; but they still risk developing chronic health effects.
- People who are not accustomed to CO exposure could easily become acutely ill from high concentrations of CO.

(D) Sulfur Dioxide (SO₂)

Sulfur Oxides (SO_x) include:

Sulfur dioxide (SO₂), and Sulfur trioxide (SO₃)

SO₂ is a criteria pollutant

Formation:

- Combustion of any S-containing material will produce SO_x;
- Oil and coal generally contain appreciable quantities of S (~ 0.5 to 6%), either in inorganic or organic form;
- When these fuels are burned, S is released mostly as SO₂, but also with small amounts of SO₃.



- Once released SO₂ can be converted to SO₃ in a series of reactions involving free radicals such as OH·



(D) Sulfur Dioxide (SO₂)

Formation (contd.):

- SO₃ reacts quickly with H₂O to form H₂SO₄, which is the principal constituent of “acid rain”.



- H₂SO₄ molecules rapidly become particles by either condensing on existing particles in the air or by merging with water vapor to form H₂O-H₂SO₄ droplets.
- Often a significant fraction of PM consists of Sulfate aerosols. Transformation of SO₂ to Sulfate particles is gradual, taking days.
- Most Sulfate particles has an effective size of < 2 μm, with most of them being in the range of 0.2 to 0.9 μm. Their size is comparable to the wavelength of visible light, and thus their presence affects visibility. Their small size also allows deep penetration into the respiratory system.

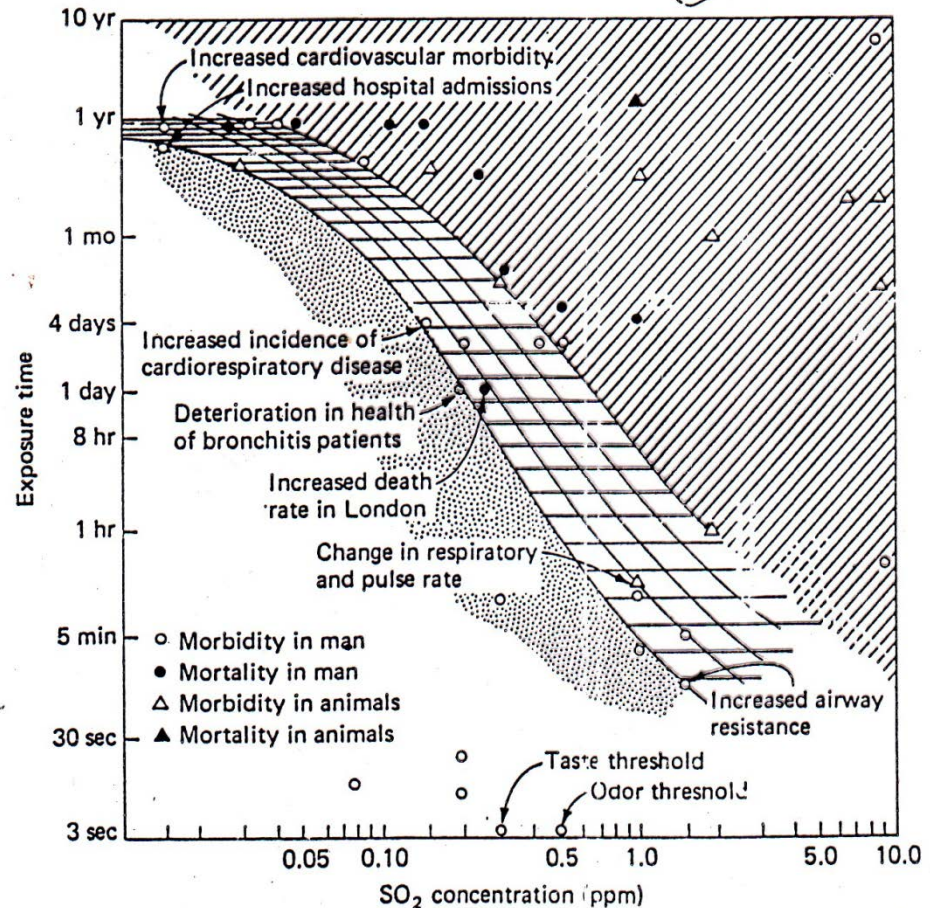
(D) Sulfur Dioxide (SO₂)

Major Sources:

- Fuel combustion in power plants and heating plants contributes the major part, accounting for about 80% of all anthropogenic SO_x emissions; combustion of coal being the primary source.
- Other industrial processes (e.g., copper smelting, petroleum refineries, sulfuric acid plants, cement manufacture) rank second.
- **Transportation contributes relatively little, because Sulfur content of gasoline is relatively low.**

(D) Health Effects of SO₂

- SO₂ is highly soluble and consequently is absorbed in the moist passages of upper respiratory system. Exposure to SO₂ ~ 1 ppm leads to constriction of the airways.
- SO₂ causes significant bronco-constrictions in asthmatics at relatively low concentrations (0.25 to 0.50 ppm)
- SO₂, H₂SO₄ and Sulfate particles irritate mucus membranes of respiratory tract and foster development of chronic respiratory diseases, e.g., bronchitis.



(D) Health Effects of SO₂ (contd.)

SO_x in dusty atmosphere:

In dusty atmosphere, SO_x is particularly harmful. Both SO₂ and H₂SO₄ paralyze the hair-like cilia, which line the respiratory tract, and pushes particulates back to throat. Without the regular sweeping action of cilia, particulates may penetrate to the lung and settle there.

These particulates usually carry with them adsorbed/absorbed SO₂, thus bringing this irritant into direct prolonged contact with delicate lung tissues.

The SO₂-Particulate combination has been cited as a cause of death in several air pollution tragedies.

(D) Sulfur Dioxide (SO₂): Effect on Materials

- H₂SO₄ aerosols attack building materials, especially those containing carbonates, such as marble, limestone, roofing slate and mortar. As a result, carbonates are replaced by sulfates, which are water soluble.



CaSO₄ formed in this way is gradually washed away by rain water, leaving pitted, discolored surface.

- Corrosion rate of most metals, esp. iron, steel, zinc, copper, nickel are accelerated by SO_x.
- H₂SO₄ mists can damage cotton, linen, rayon and nylon. SO_x also damages paper and leather.

(E) Nitrogen Dioxide (NO₂)

Nitrogen Oxides (NO_x) of primary concern in atmospheric pollution include:

Nitric oxide (NO), and Nitrogen dioxide (NO₂)

NO₂ is a criteria pollutant

Formation NO_x:

Two types of NO_x are formed during combustion:

- (1) Thermal NO_x:** created when N and O in the combustion air are heated to high temperature (> 1000 K) to oxidize N
- (2) Fuel NO_x:** result from oxidation of nitrogen compounds that are chemically bound in the fuel molecules themselves. Coal has about 3% N by weight; natural gas has almost none.

(E) Nitrogen Dioxide (NO₂)

Major Sources:

- **Fuel combustion in stationary sources (power plants, heating plants).**
- **Vehicular emissions.**
- **Other sources e.g., industrial processes (nitric acid plant).**

(E) Effects of Nitrogen Dioxide (NO₂)

- Almost all NO_x emissions are in the form of NO, which has no known adverse health effects at concentrations commonly found in air (~ 1 ppm).
- NO can be oxidized to NO₂ ($\text{NO} + \frac{1}{2}\text{O}_2 = \text{NO}_2$); NO₂ may react with Hydrocarbon in the presence of sunlight to form “photochemical smog”, which is injurious.
- NO₂ also reacts with Hydroxyl Radical (OH·) in the atmosphere to form nitric acid (HNO₃), which is washed out of the atmosphere as “acid rain”. It also forms “nitrate particles” in the atmosphere.
- NO₂ irritates lung; persistent low level concentrations of NO₂ increases respiratory illness.
- NO₂ can cause damage to plants; and when converted to HNO₃, it leads to corrosion of metals.

(F) Photochemical Smog and Ozone (O₃)

Formation:

When NO_x, various Hydrocarbons (HCs, such as CH₄) and Sunlight come together, they can initiate a complex set of reactions to produce a number of secondary pollutants known as “photochemical oxidants” or “photochemical smog”. It mainly occurs in highly motorized areas in large metropolitan cities.



Constituents of Photochemical Smog/Oxidants:

- Ozone (most abundant), **a criteria pollutant**
- Formaldehyde
- Peroxy-benzyl-nitrate (PBzN)
- Peroxy-acetyl-nitrate (PAN)
- Acrolein
- Other organic constituents

(F) Effects of Photochemical Smog

- Ozone is a powerful oxidizing agent and affects human health, for example by causing oxidative stress in lungs.
- Ozone is responsible for chest constriction and irritation of mucus membrane.
- Eye irritation, the most common complaint about smog, is caused by components of “smog” (e.g. formaldehyde, acrolein, PAN) other than Ozone.
- Ozone is also the most important air pollutant responsible for reducing crop yields. Implementation of a range of CH₄ abatement measures globally is expected to prevent yearly yield loss of about 25 million tons of four staple crops (maize, rice, soybean and wheat) (UNEP/WMO, 2011).

Photochemical Smog and Ozone:

(a) NO-NO₂-O₃ Photochemical Reaction Sequence



If sunlight is available, NO₂ can photolyze and the freed atomic oxygen (Eq. 3) can then help to form O₃.

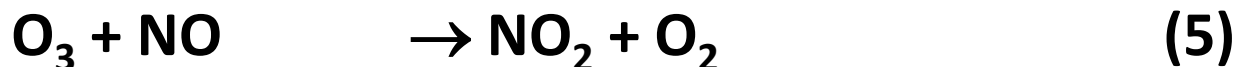


where, $h\nu$ = a photon

M = a molecule, usually O₂ or N₂

Presence of M is necessary to absorb excess energy from the reaction. Without M, O₃ would have too much energy to be stable, and it would dissociate back to O and O₂.

O₃ can then convert NO back to NO₂ as follows:



Photochemical Smog and Ozone:

(a) NO-NO₂-O₃ Photochemical Reaction Sequence

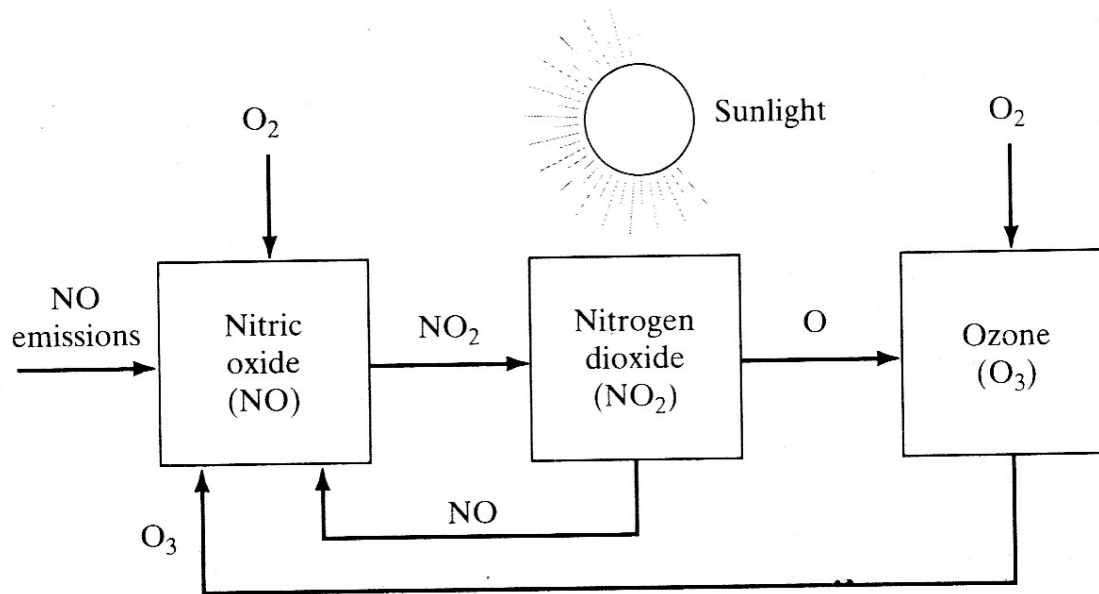


FIGURE 7.7 Simplified atmospheric nitrogen photolytic cycle.

If these were the only reactions, there would be no net change in concentration of NO, NO₂ and O₃ over time.

Photochemical Smog and Ozone:

(a) NO-NO₂-O₃ Photochemical Reaction Sequence

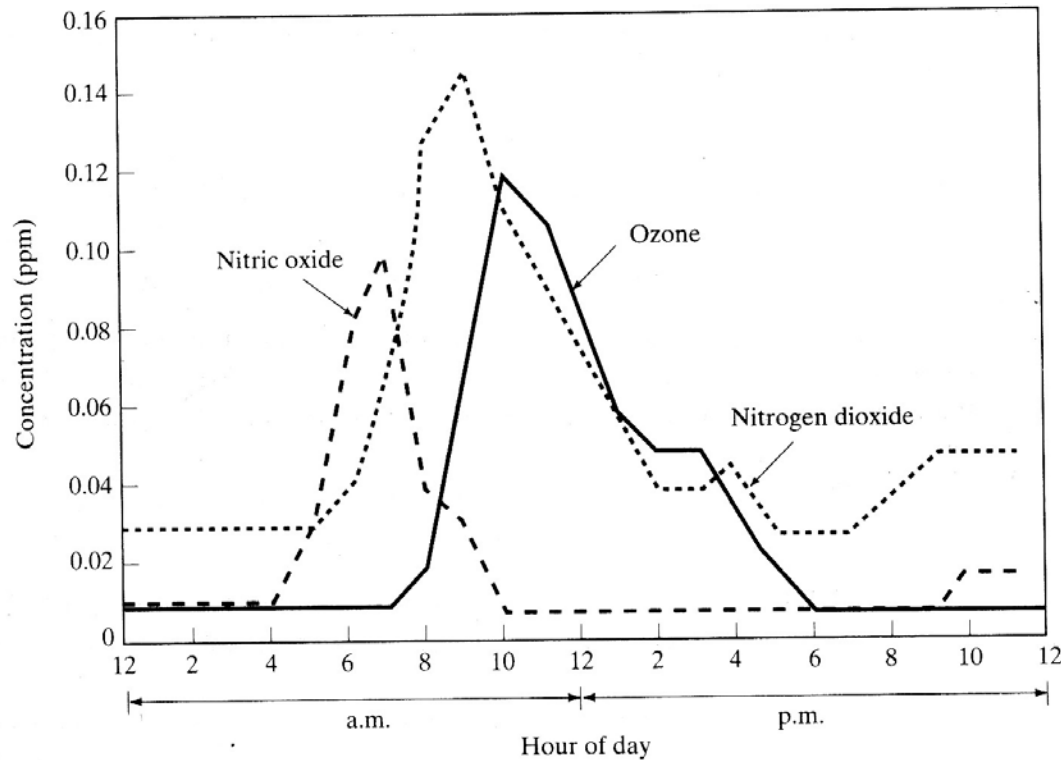


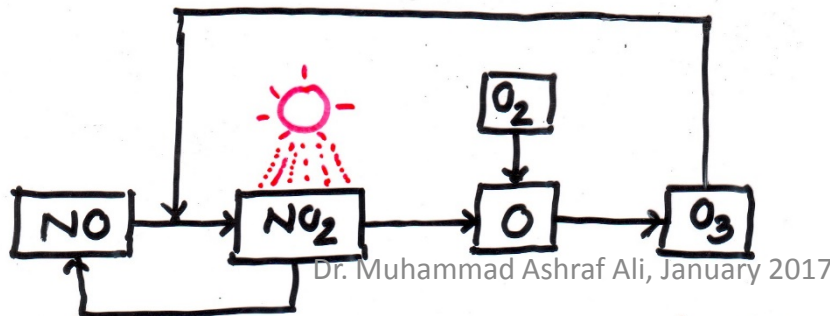
FIGURE 7.8 Diurnal variation of NO, NO₂, and O₃ concentrations in Los Angeles on July 19, 1965. (Source: U.S. HEW, 1970)

However, observed O₃ concentrations are often much higher than that predicted by the nitrogen cycle alone.

Photochemical Smog and Ozone:

(b) NO-NO₂-O₃ Photochemical Reaction Sequence

- The availability of NO₂ affects the rate of production of O₃, while the availability of NO affects the rate of destruction of O₃.
- Any reaction that will help convert NO to NO₂ will increase O₃ concentration both by:
 - (a) reducing the amount of NO available to destroy O₃, and
 - (b) increasing the amount of NO₂ available to create O₃
- By introducing certain types of HCs into the nitrogen photolytic cycle, the balance of production and destruction of O₃ can be upset, allowing more O₃ to accumulate in the air (next slides)



Photochemical Smog and Ozone:

(b) Hydrocarbon-NO_x-O₃ Reaction Sequence

The chemistry of photochemical smog is very complex. The following section provides some insight about the formation of photochemical smog:

Formation of OH· Radical:



OH· radical plays an important role in the atmospheric organic chemistry. Important reactions involving OH· include oxidation of NO₂ to HNO₃, and CO to CO₂.

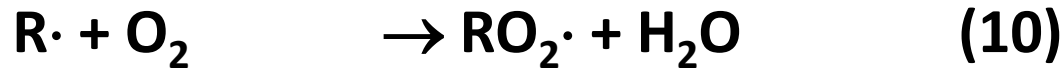
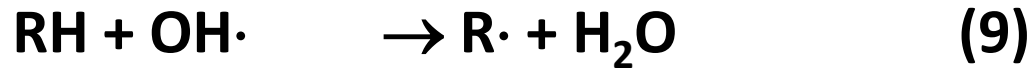


Photochemical Smog and Ozone:

(b) Hydrocarbon-NO_x-O₃ Reaction Sequence

Conversion of NO to NO₂: Role of Hydrocarbons:

Consider Hydrocarbon: RH [R· = C_nH_{2n+1} (alkyl radical)]



Thus, Hydrocarbons can help convert NO to NO₂, and thus increase O₃.

But the above reaction cycle depends on the presence of OH·, whose concentration in the atmosphere is very small.

Photochemical Smog and Ozone:

(b) Hydrocarbon-NO_x-O₃ Reaction Sequence

Conversion of NO to NO₂: Role of Hydrocarbons:

Hence, for conversion of NO to NO₂ to continue, there has to be a way to rejuvenate OH· radical. This can happen according to the following reactions:



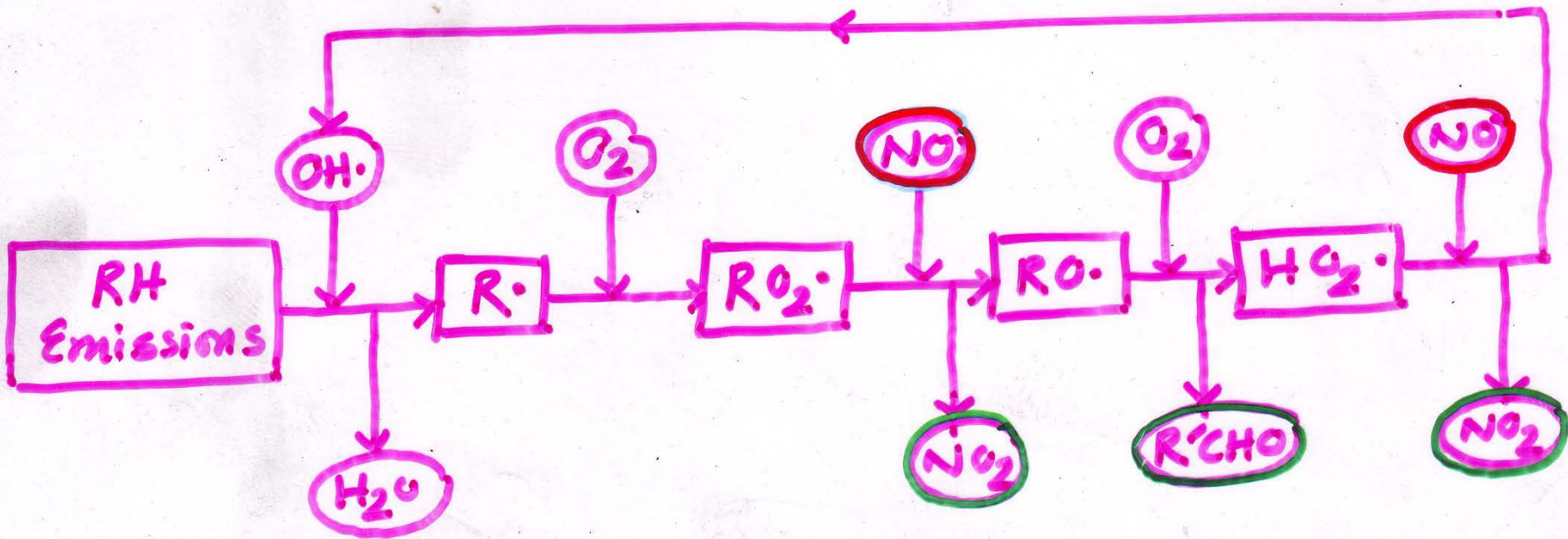
Net effects of Eq. 9-13:

- One hydrocarbon (RH) converts two molecules of NO into NO₂ and produces an aldehyde (a component of photochemical smog).
- This increases O₃ concentration by: (a) reducing the amount of NO available to destroy O₃; and (b) increasing the amount of NO₂ available to create O₃.

Photochemical Smog and Ozone:

(b) Hydrocarbon-NO_x-O₃ Reaction Sequence

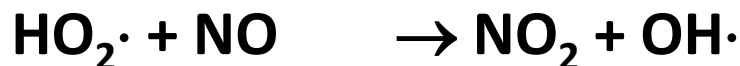
Conversion of NO to NO₂ by Hydrocarbon:



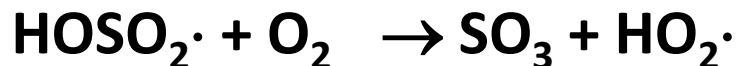
Photochemical Smog and Ozone

A number of other common air pollutants also promote conversion of NO to NO₂.

Conversion of NO to NO₂ by CO:

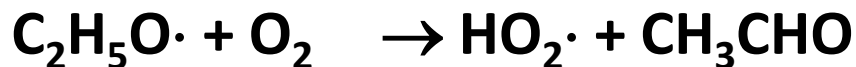
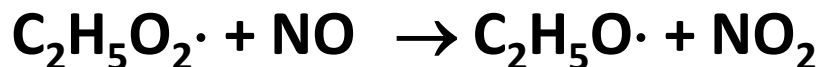
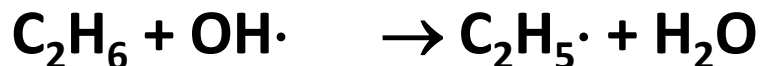


Conversion of NO to NO₂ by SO₂:



Photochemical Smog and Ozone

Formation of Acetaldehyde from Ethane:



CH₃CHO is an aldehyde call Acetaldehyde. It plays a role in the formation of eye irritant peroxy-acetyl-nitrate (PAN).