

# LECTURE 8: SOURCES AND CHARACTERISTICS OF MAJOR AIR POLLUTANTS

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CE 433

Excerpts from Lecture notes of Professor M. Ashraf Ali, BUET.

# Particulates/Particulate Matter (PM)/Aerosol

- Consists of any dispersed matter in the air, solids or liquid (except pure water), with size ranging from molecular clusters of 0.005  $\mu\text{m}$  to coarse particles of up to 100  $\mu\text{m}$ .
- 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: 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)

- Size of PM: Aerodynamic Diameter:
  - Particles of most interest have aerodynamic diameter in the range 0.1 to 10  $\mu\text{m}$ . Particles smaller than these undergo random (Brownian) motion and through coagulation generally grow to sizes  $> 0.1\mu\text{m}$ . Particles larger than 10  $\mu\text{m}$  settle quickly.
  - Fine Particulates:  $\text{PM}_{2.5}$
  - Coarse Particulates:  $\text{PM}_{2.5-10}$
  - Submicron Particulates:  $\text{PM}_1$
- Distribution and Characteristics of PM:
  - 90% in earth's atmosphere, 10% anthropogenic
  - Most natural particles are harmless, particles of anthropogenic sources are toxic
  - Particulates of anthropogenic sources are considered more harmful because of their
    - a) Non-uniform distribution; b) chemical composition ; c) size distribution

# Sources of Particulates: Global Scale

Natural Sources	Global Emission (X 10 <sup>12</sup> ) g/yr
Soil & Rock Erosion	50-250
Forest Fire	1-50
Sea Spray	300
Volcanoes	25-150
Secondary particles (formed from gaseous emissions of H <sub>2</sub> S, NH <sub>3</sub> , NO <sub>x</sub> , HC etc)	345-1100
<b>TOTAL</b>	<b>721-1850</b>

Anthropogenic Sources	Emission in US (X 10 <sup>12</sup> ) g/yr
Industrial Processes (Stationary sources, fossil fuel)	10
Transportation	1.3
Fugitive emission from industry	3.3
Fugitive emission from non-industrial activity (eg, road dust, construction, agricultural)	110-370
<b>TOTAL</b>	<b>125-385</b>

# Composition of particulates

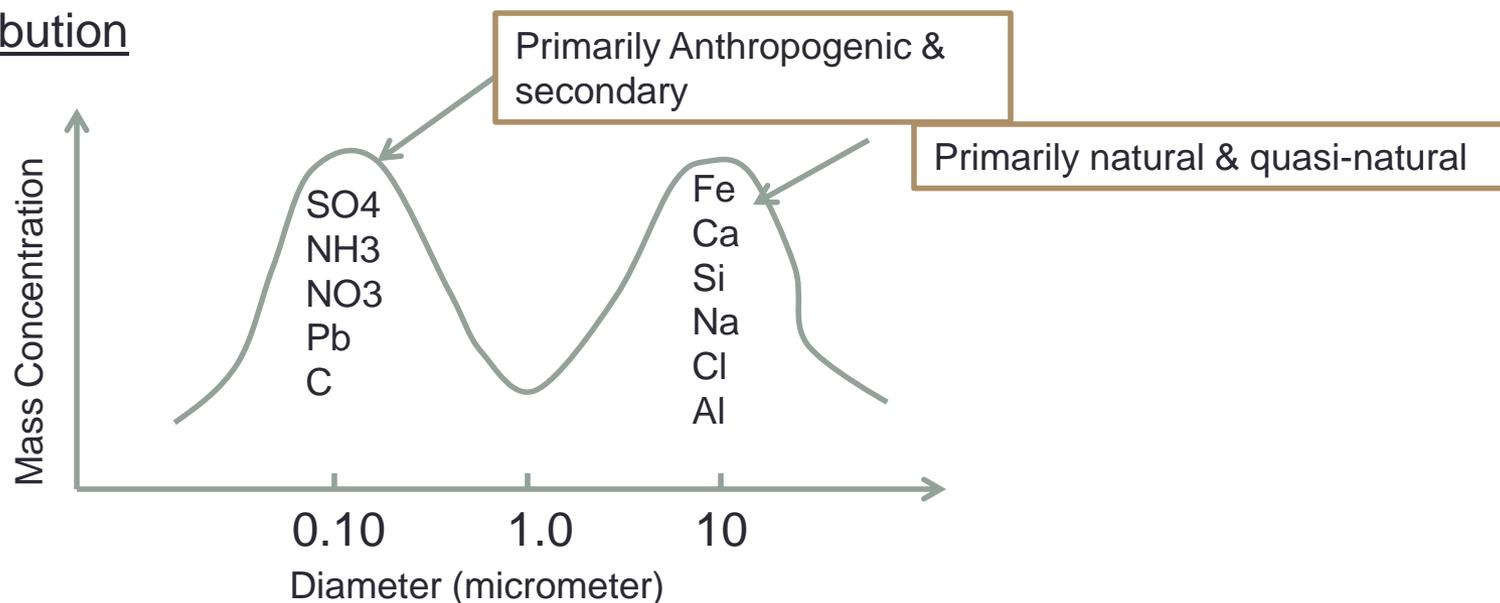
- About 40 elements can be found in particulates.
- Most important elements include:

Al, Fe, Na, Si ----- mostly of natural origin.

(Soil: 8% Al, 6% Fe)

C, S, Pb, V, Ni, As, Ag, Cu, Cd – mostly of anthropogenic origin.

- Size Distribution



**Figure: Idealized aerosol mass distribution showing a typical segmentation of chemical chemical species into fine and coarse fractions**

# Particulates in Urban Environments: Source Apportionment of Particulate Matter in Dhaka

- Average Mass contribution to Particulate Pollution in Dhaka, 1993-94 (%)
- Based on Biswas et al. (2006)

Source Type	Coarse (PM <sub>10</sub> )	Fine (PM <sub>2.5</sub> )
Re suspended Soil	64.7	8.88
2-stroke engine	6.07	2.03
Construction works	7.09	-
Motor Vehicles	31.2	29.1
Sea Salt	0.22	4.11
Refuse burning	0.74	-
Natural gas/diesel burning	-	45.7
Metal Smelting	-	10.2

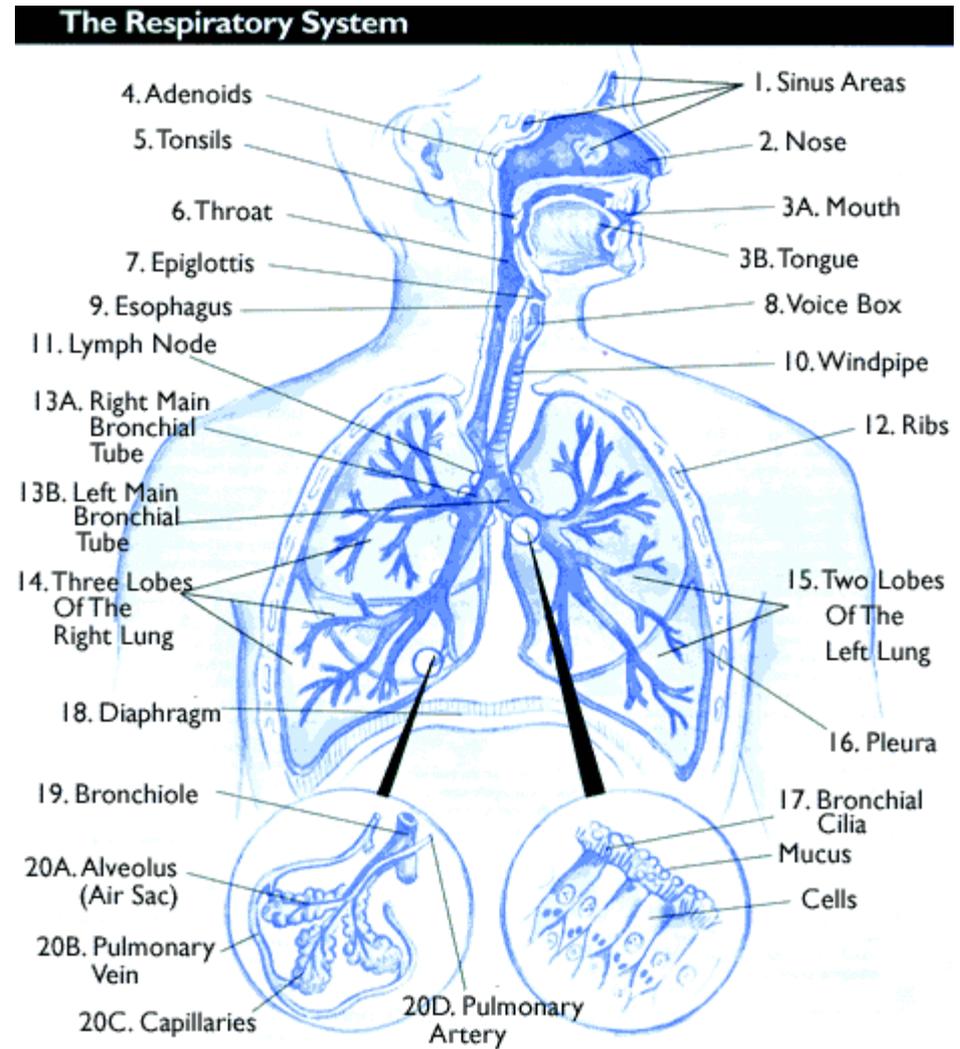
- Other Studies
  - Major Sources of PM<sub>2.5</sub> : Motor Vehicle, Brick kiln, road dust/soil dust
  - Major sources of PM<sub>10</sub> : Soil dust, Motor Vehicle, road dust, saw dust

# Health Effects of Particulates

- Particles (aerosols) suspended in the air enter our body when we breathe. These particles include:
  - Natural particles (eg., bacteria, viruses, pollen, sea salt, road dust)
  - Anthropogenic emissions (e.g. cigarette smoke, vehicle exhaust etc.)
- The hazard posed by these particles depends on their chemical composition as well as where they deposit within our respiratory system.
- Hence we need to learn about our respiratory system

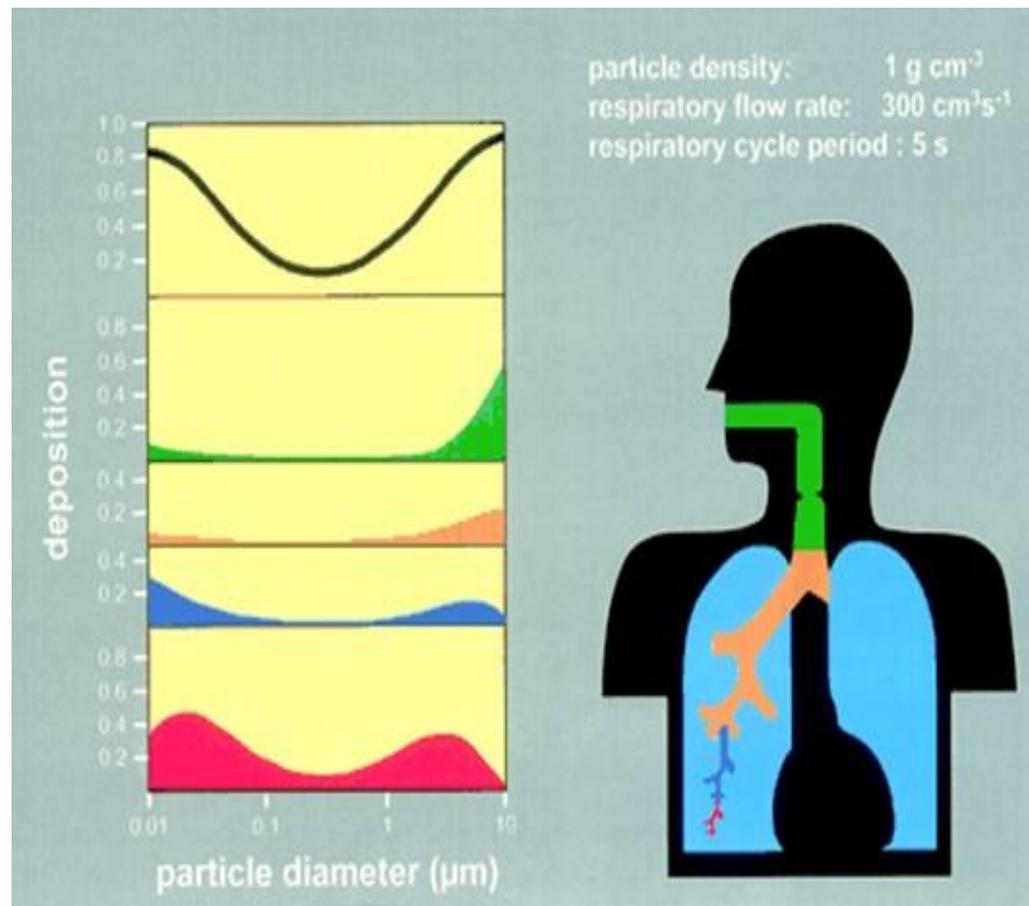
# Deposition of particles in the respiratory system (Figure)

- Upper Respiratory System:
  - Nasal Cavity, Trachea
- Lower Respiratory System:
  - Bronchial Tubes, Lungs



From the viewpoint of respiratory deposition of particulates, the respiratory system can be divided into three regions

- Head Airways Region
  - Nasal airway
  - Oral airway
- Lung Airways Region (Tracheobronchial Region)
  - From trachea to terminal bronchioles (23 branchings)
- Pulmonary Region
  - Across the alveolar membrane  $O_2$  and  $CO_2$  counter-diffuse
  - Surface area (if fully unfolded)  $\sim 75 \text{ m}^2$



# Respiratory Deposition

- Large particles entering the respiratory system can be trapped by hairs and lining of the nose. Once captured they can be driven out by cough and sneeze
- The nasal path is usually more efficient at removing particles than the oral path. Deposition of particles in the head region during inhalation by nose is essentially total for particles with diameter  $> 10 \mu\text{m}$ . During mouth breathing, however, the upper size cutoff for particles penetrating beyond the head region is  $15 \mu\text{m}$ .
- Smaller particles that make it into the tracheobronchial system (lung airways) can be captured by mucus, worked back to throat by the tiny hair-like “cilia” and removed by swallowing or spitting. The muco-ciliary transport can get the deposited particles out of the respiratory system in a matter of hours.

# Respiratory Deposition (contd.)

- Smaller particles are often able to traverse deeper without being captured in the mucus lining, but depending on their size they may or may not be deposited there. Some particles are so small that they tend to follow the air stream into the lung and then right back out again.
- The alveolar region does not have the muco-ciliary mechanism (because it is designed for gas exchange). It takes months or years to clear the insoluble particles deposited in this region.
- Fibrogenic dusts, such as silica, asbestos and coal dust interfere with the cleaning mechanism resulting in “fibrosis” of the region. Insoluble radioactive materials deposited in this region may cause subsequent damage due to long retention time and subsequently continuous radiation.
- Soluble materials can pass through the alveolar membrane and be transported to other parts of the body. Hence it is the region where viruses invade and it is also the target region for therapeutic aerosol delivery.

# Particle Deposition Mechanism

- Most important Mechanisms are:

- 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 important mechanism in bronchial region.

- Settling

When flow velocity is small and the airway dimension is small, gravitational settling becomes an important deposition mechanism for large particles. It is especially important for horizontally oriented airways

# Particle Deposition Mechanism

- Diffusion/Brownian motion

In the small airways, where the distance is short and the residence time is long, diffusion is an important mechanism for the deposition of small particles ( $<0.5 \mu\text{m}$ ). It induces movement of particles from a high concentration region (in this case, the centre of air stream) to a lower concentration region (in this case, the airway wall). The effectiveness of this mechanism increases as particle size decreases.

- 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.

# Total Deposition of Particles

- A particle entering our respiratory system is subject to **all the deposition mechanisms**. Several models have been developed to predict the deposition based on **experimental data**. The total deposition fraction (DF) in the respiratory system according to [International Commission on Radiological Protection \(ICRP\)](#) model is

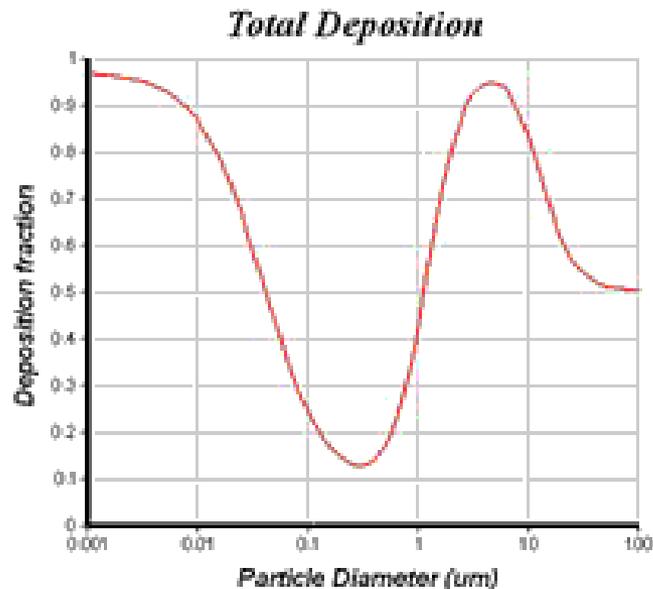
$$DF = IF \left( 0.0587 + \frac{0.911}{1 + \exp(4.77 + 1.485 \ln d_p)} + \frac{0.943}{1 + \exp(0.503 + 2.58 \ln d_p)} \right)$$

- where  $d_p$  is particle size in  $\mu\text{m}$ , and IF is the inhalable fraction defined as

$$IF = 1 - 0.5 \left( 1 - \frac{1}{1 + 0.00076 d_p^{2.8}} \right)$$

# Total Deposition of Particles

Large particles have a high deposition fraction due to impaction and settling. The fraction decreases for particles larger than  $3\mu\text{m}$  is due to the reduced entry into the mouth or nose. Small particles also get a high deposition fraction due to diffusion. The minimum efficiency is between  $0.1$  and  $1.0\ \mu\text{m}$ , where none of the above mechanisms dominates.



# Regional Deposition

- Regional deposition is of more interest because it's more relevant in assessing the potential hazard of inhaled particles and the effectiveness of therapeutic delivery. The deposition fraction in the three regions can be approximated by the following equations:

For the **Head Airways**,

$$DF_{HA} = IF \left( \frac{1}{1 + \exp(6.84 + 1.183 \ln d_p)} + \frac{1}{1 + \exp(0.924 - 1.885 \ln d_p)} \right)$$

For the **Tracheobronchial region**,

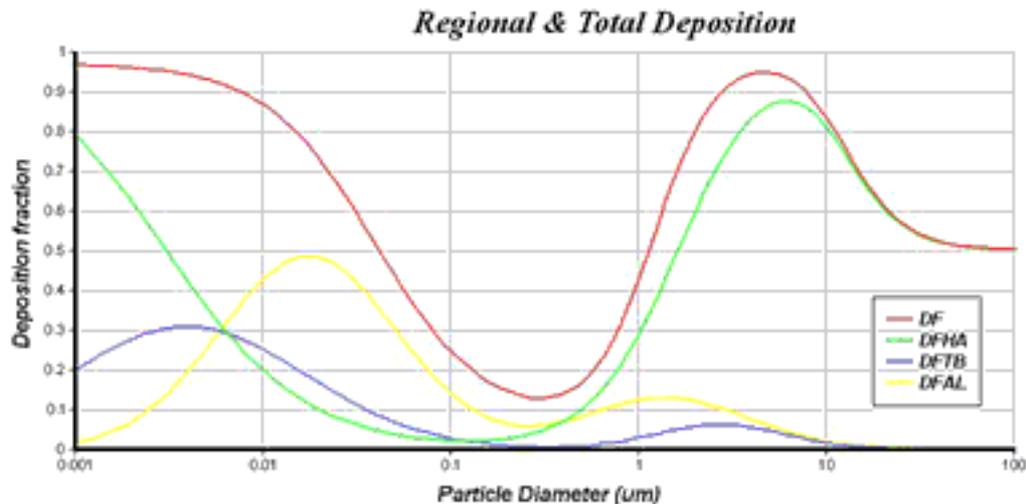
$$DF_{TB} = \left( \frac{0.00352}{d_p} \right) [\exp(-0.234(\ln d_p + 3.40)^2) + 63.9 \exp(-0.819(\ln d_p - 1.61)^2)]$$

For the **Alveolar region**,

$$DF_{AL} = \left( \frac{0.0155}{d_p} \right) [\exp(-0.416(\ln d_p + 2.84)^2) + 19.11 \exp(-0.482(\ln d_p - 1.362)^2)]$$

# Regional Deposition

- The largest particles are removed by settling and impaction in the **Head Airways**. Ultrafine particles less than  $0.01\ \mu\text{m}$  can also have significant deposition in this region due to their high diffusivity
- In the **Tracheobronchial region**, impaction and settling are important for particles larger than  $0.5\ \mu\text{m}$  although the overall deposition fraction in this size range is quite small
- Particles entering the **Alveolar region** have high deposition efficiency no matter they are larger or small: settling for large particles and diffusion for small particles



# Health Effects of Particulates

- Extent of effect depends on size and concentration, presence of other contaminants (e.g. SO<sub>x</sub>), length of exposure, chemical composition and where they deposit in the respiratory system
- Exposure to particulate matter is associated with increased incidence of respiratory illness, chronic bronchitis, broncho-constriction, decrement in pulmonary function and increased mortality rates.
- Adverse effects associated with short-term exposure to particulate matter include increases in the rate of asthma attack.

# Lead (Pb)

- 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 food stuff.
- About 1/3 of lead particles inhaled are deposited in the respiratory system, and about 1/2 of those are absorbed by bloodstream.
- Adverse effect of lead poisoning include aggressive, hostile and destructive behavioral changes, learning disabilities, seizures, severe and permanent brain damage and even death
- Vulnerable group include children and pregnant women.
- Other sources of Pb:  
Paint, Food processing, Coal combustion/metal smelting, plants manufacturing lead acid batteries and plumbing

# Carbon Monoxide (CO)

- Formation of CO:

- Incomplete combustion of carbon/carbon containing fuel



- Industrial production of CO by high temperature reaction between  $\text{CO}_2$  and carbon containing material



- Sources of CO:

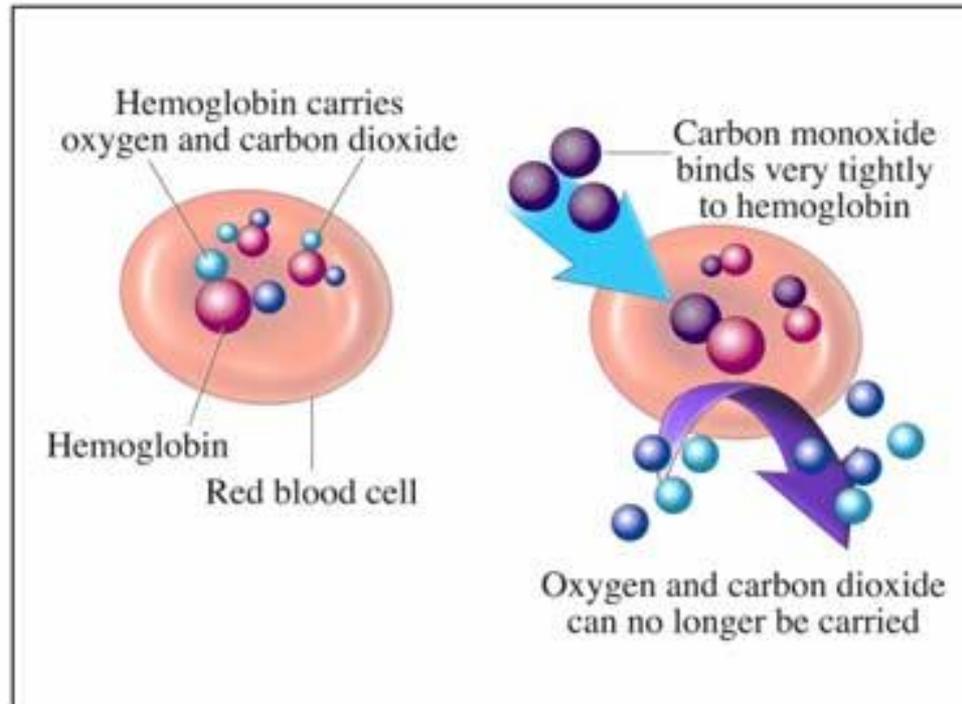
- Transportation (most significant, often accounts of most of the CO emission in urban areas)
- Industrial processes
- Miscellaneous
- Natural (e.g. volcanic activity)

# Health Effects of CO

- The effects of CO exposure are reflected in the O<sub>2</sub> carrying capacity of blood.
- In normal functioning, hemoglobin (Hb) molecules carry oxygen which is exchanged for CO<sub>2</sub> in the capillaries connecting arteries and veins
- CO diffuses through the alveolar wall and competes with O<sub>2</sub> for one of the 4 iron sites in hemoglobin molecule. Affinity of the iron site for CO is about 210 times greater than for O<sub>2</sub>.
- When a hemoglobin molecule acquire a CO molecule, it is called carboxyhemoglobin.
- Formation of COHb causes two problems:
  - (1) less sites for O<sub>2</sub>
  - (2) greater amount of energy binding 3 O<sub>2</sub> molecules to Hb, so that they cannot be released easily (to be exchanged for CO<sub>2</sub>).

Note: Formation of COHb is a reversible process, with a half-life for dissociation after exposure of about 2 to 4 hr for low concentrations.

# Health Effects of CO



# Health effects of CO

- CO concentration in busy roadways often range from 5 to 50 ppm, CO concentration of ~100 ppm has also been recorded
- 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 and charcoal combustion in developing countries can be between 100 to 200 ppm, with peak concentration as high as 400 ppm lasting for several hours.
- People who are consistently exposed to high levels of CO, like heavy smokers or women in traditional 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 concentration of CO.

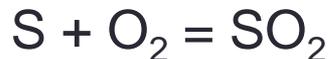
# Sulfur Oxides

- Pollution from sulfur oxides consist primarily of two colorless gaseous compounds: Sulfur dioxide,  $\text{SO}_2$  sulfur trioxide,  $\text{SO}_3$ 
  - Collectively these two are referred to as “ $\text{SO}_x$ ”

- Formation:

The combustion of any s-containing material will produce both sulfur oxides. Oil and coal generally contain appreciable quantities of sulfur (~0.5 – 6%), either in the form of inorganic sulfides or as organic sulfur

When these fuels are burnt, sulfur is released mostly as sulfur dioxide ( $\text{SO}_2$ ), but also with small amounts of  $\text{SO}_3$ .



- $\text{SO}_2$  once released can convert to  $\text{SO}_3$  in a series of reactions involving free radical such as  $\text{OH}^\cdot$
- $\text{SO}_3$  reacts quickly with  $\text{H}_2\text{O}$  to form  $\text{H}_2\text{SO}_4$ , which is the principal cause of “acid rain”



# Sulfur Oxides

- Sulfuric acid molecules rapidly become particles by either condensing on existing particles in the air or by merging with water vapor to form  $\text{H}_2\text{O}-\text{H}_2\text{SO}_4$  droplets.
- Often a significant fraction of particulate matter in the atmosphere consists of such sulfate ( $\text{SO}_4^{2-}$ ) aerosols. The transformation of  $\text{SO}_2$  gas to sulfate particles is gradual, taking days.
- Most sulfate particles in urban air have an effective size of less than  $2\mu\text{m}$  – with most of them being in the range of 0.2 to 0.9  $\mu\text{m}$ . Their size is comparable to the wavelengths of visible light and their presence greatly affects visibility.
- Their size also allows deep penetration into the respiratory system.

# Major Sources of SO<sub>x</sub>: Global scale

- Fuel combustion in power plants and heating plants contributes the major part, accounting for about 80% of all man-made SO<sub>x</sub> emissions ; combustion of coal being the primary source.
- Other industrial processes (e.g. copper smelting, petroleum refineries, sulfuric acid plant, cement manufacture) rank second to stationary sources (i.e. power plant and heating plant), with about 16% of total emissions.
- Transportation contributes relatively little, because sulfur-content of gasoline is relatively low.

# Health Effects of $\text{SO}_x$ :

- $\text{SO}_2$  is highly soluble and consequently is absorbed in the moist passages of the upper respiratory system. Exposure to  $\text{SO}_2$  levels of the order of 1 ppm leads to constriction of the airways in the respiratory tract.  $\text{SO}_2$  causes significant broncho-constrictions in asthmatics of relatively low to concentrations (0.25 to 0.5 ppm)
- $\text{SO}_2$  ,  $\text{H}_2\text{SO}_4$  and sulfate salts tend to irritate the mucus membranes of respiratory tract and faster development of chronic respiratory disease, e.g. bronchitis.
- In dusty atmosphere,  $\text{SO}_x$  is particularly harmful. Because both  $\text{SO}_2$  and  $\text{H}_2\text{SO}_4$  paralyze the hair-like cilia which line the respiratory tract without regular sweeping action of cilia particulates may penetrate to the lung and settle there. These particulates usually carry absorbed/adsorbed  $\text{SO}_2$ , thus bringing this irritant into direct prolonged contact with delicate lung tissues. The  $\text{SO}_2$ - particulate combination has been cited as cause of death in several air pollution tragedies.

# Effects of SO<sub>x</sub> on Materials

- H<sub>2</sub>SO<sub>4</sub> aerosols readily attack building materials, especially those containing carbonates such as marble, limestone, roofing slate and mortar.
- The carbonates are replaced by sulphates which are water soluble according to the following equation:



The CaSO<sub>4</sub> formed in this process is washed away by rain water leaving a pitted discolored surface.

- Corrosion rates of most metals, esp steel, zinc, copper, nickel are accelerated by SO<sub>x</sub> polluted environments
- H<sub>2</sub>SO<sub>4</sub> mists can also damage cotton, linen, rayon and nylon.
- Leather weakens and disintegrates in the presence of excess SO<sub>x</sub> by-products.
- Paper absorbs SO<sub>2</sub>, which is oxidized to H<sub>2</sub>SO<sub>4</sub> ; the paper turns yellow and becomes brittle. This is why many industrialized cities store historic documents in carefully controlled environment.
- SO<sub>2</sub> damages trees.

# Oxides of Nitrogen ( $\text{NO}_x$ )

Nitric Oxide (NO) and Nitrogen dioxide ( $\text{NO}_2$ ) are of primary concern in atmospheric pollution

- Formation of  $\text{NO}_x$ :

Two sources of  $\text{NO}_x$  during combustion of fossil fuel

- 1) Thermal  $\text{NO}_x$ : Created with N and O in the combustion air are heated to high temperature ( $>1000\text{K}$ ) to oxidize N.
- 2) Fuel  $\text{NO}_x$ : Result from oxidation of nitrogen compounds that are chemically bound in the fuel molecules themselves. (Note: coal has about 3% N by weight, natural gas has almost none)

- Sources of  $\text{NO}_x$ :

1) Natural sources:  $\text{NO}_x$  produced by

- solar radiation
- lightening and forest fire
- bacterial decomposition of organic matter

2) Anthropogenic Sources: Global scale

- fuel combustion in stationary sources (~49%)
- automobile exhaust (~39%)
- other sources eg. Industrial processes (nitric acid plant), etc.

# NO<sub>x</sub> in Urban Environment

- Source Contributions to emissions of NO<sub>x</sub> in greater Mumbai (1992) (WB, 1996)

Sources	NO <sub>x</sub> (%)
Power Plant	30
Gasoline Vehicles	18
Diesel Vehicles	34
Industrial fuel	11
Domestic fuel	4
Marine	3

# Effects of NO<sub>x</sub>

- Almost all NO<sub>x</sub> emissions are in the form of NO, which has no known adverse health effects at concentrations found in atmosphere (~<1 ppm)
- NO can be oxidized to NO<sub>2</sub> ( $\text{NO} + \frac{1}{2} \text{O}_2 = \text{NO}_2$ ), which may react with hydrocarbons in the presence of sunlight to form photochemical smog. That is injurious.
- NO<sub>2</sub> also reacts with hydroxyl radical (HO) in the atmosphere to form nitric acid (HNO<sub>3</sub>), which is washed out of the atmosphere as acid rain.
- NO<sub>2</sub> irritates lung.
- Persistent low level concentration of NO<sub>2</sub> increases respiratory illness
- NO<sub>2</sub> can cause damage to plants and when converted to HNO<sub>3</sub>, it leads to corrosion of metal surface.

# Photochemical Smog and Ozone

- When  $\text{NO}_x$ , various hydrocarbons and sunlight come together, they can initiate a complex set of reactions to produce a number of secondary pollutants known as “photochemical oxidant”

**Hydrocarbons +  $\text{NO}_x$  + sunlight  $\rightarrow$  Photochemical smog**

- Constituent of smog:
  - Ozone (most abundant), formaldehyde, peroxybenzoyl nitrate (PBZN), peroxy acetyl nitrate (PAN), acrolein etc.
- Ozone ( $\text{O}_3$ ) is primarily responsible for chest constriction irritation of mucus membrane, cracking of rubber, damage to vegetation
- Eye irritation, the most common complaint about smog, is caused by the other components of smog listed above [esp. formaldehyde ( $\text{HCHO}$ ) and acrolein ( $\text{CH}_2\text{CHCHO}$ ), PAN].
- Photochemical smog mainly occurs in highly motorized areas in large metropolitan cities

# Photochemical Smog and Ozone

- NO-NO<sub>2</sub>-O<sub>3</sub> Photochemical Reaction Sequence: (Without Considering Hydrocarbon)



- If Sunlight is available, NO<sub>2</sub> can photolyze, and the freed atomic oxygen can then help to form O<sub>3</sub>



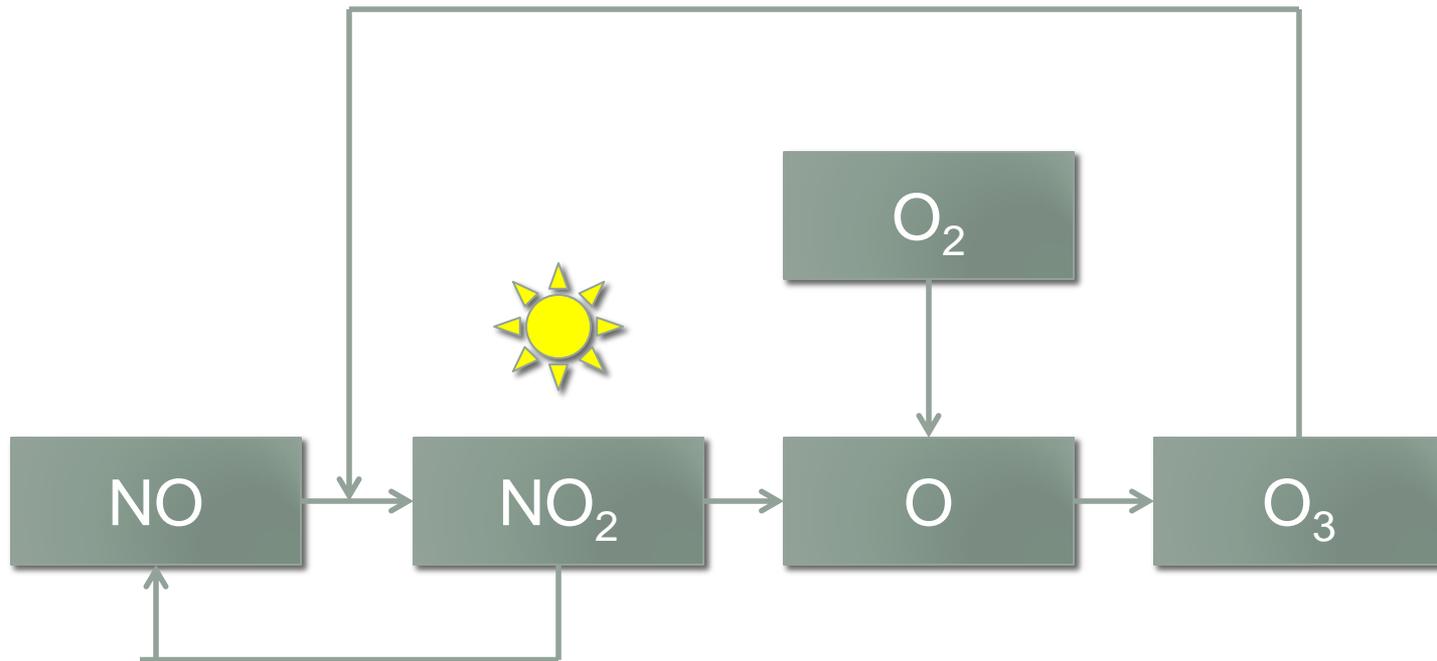
Where,  $h\nu$  = a photon

M = a molecule, usually O<sub>2</sub> or N<sub>2</sub>

- Presence of M is necessary to absorb excess energy from the reaction. Without M, O<sub>3</sub> would have too much energy to be stable, and it would dissociate back to O and O<sub>2</sub>.
- O<sub>3</sub> can then convert NO back to NO<sub>2</sub> :



# Simplified atmospheric nitrogen photolytic cycle



# Typical diurnal variation of NO, NO<sub>2</sub> and O<sub>3</sub>

- Early morning: Rising NO concentration as traffic emits NO
- As morning progresses: A drop in NO and rise in NO<sub>2</sub>, as NO gets converted to NO<sub>2</sub>
- Noon: In the presence of sun, NO<sub>2</sub> begins to drop, while O<sub>3</sub> increases
- Rest of the day: O<sub>3</sub> is so effective in its reaction with NO that as long as there is O<sub>3</sub> present, NO concentrations do not rise during the rest of the afternoon even though there may be new emissions
- If there were the only reactions, there would be no net change in the concentration of NO, NO<sub>2</sub> and O<sub>3</sub> over time
- However, observed O<sub>3</sub> concentrations are often much higher than that predicted by the nitrogen photolytic cycle alone.

# Typical diurnal variation of NO, NO<sub>2</sub> and O<sub>3</sub>

- The availability of NO<sub>2</sub> affects the rate of production of O<sub>3</sub>, while the availability of NO affects the rate of destruction of O<sub>3</sub>
- Any reaction that will help convert NO to NO<sub>2</sub> will increase O<sub>3</sub> concentration both
  - by reducing the amount of NO available to destroy O<sub>3</sub>, and
  - By increasing the amount of NO<sub>2</sub> available to make O<sub>3</sub>
- By introducing certain types of hydrocarbons into the nitrogen photolytic cycle, the balance of production and destruction of O<sub>3</sub> can be upset, allowing more O<sub>3</sub> to accumulate in air.