ENSC 412 *Air Pollution*

Lecture Week 2

Natural vs Polluted Atmosphere, Scales of Air Pollution

Readings this week

- Fenger (2009). Air Pollution in the last 50 years

The Unpolluted Atmosphere - overview

The natural and polluted atmosphere

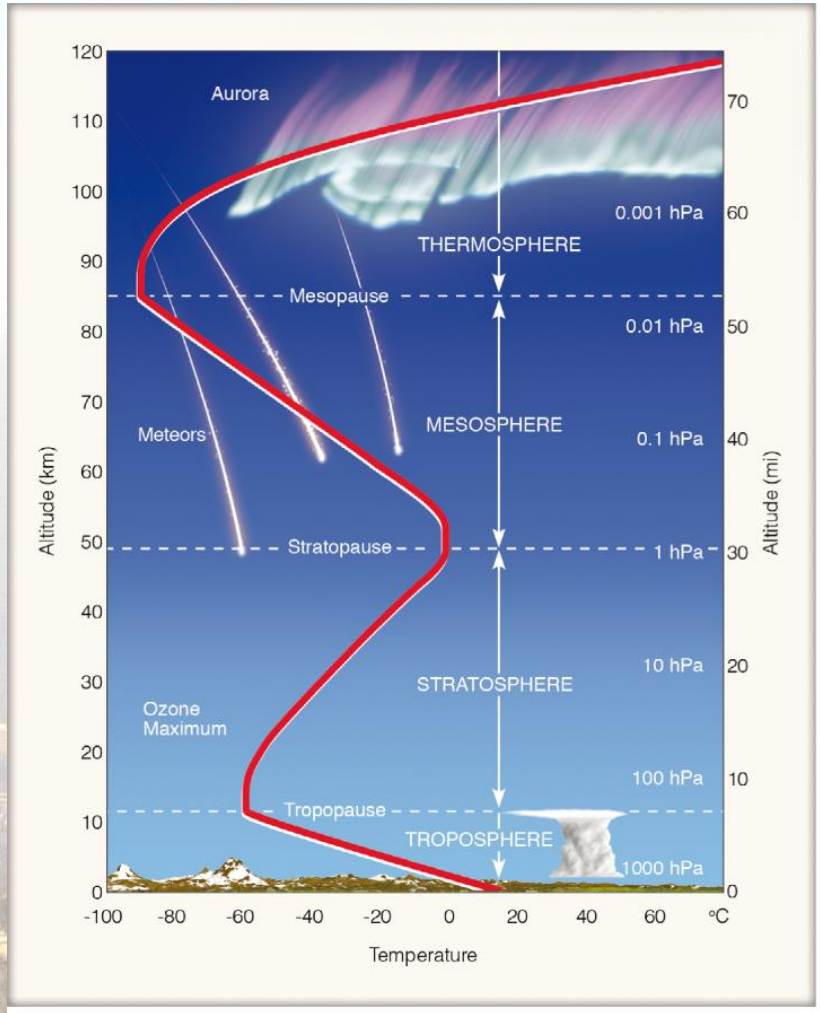


FIGURE 1.11 Thermal layers of the atmosphere as defined by the average air temperature profile (heavy line) above Earth's surface.

- Vertical Structure

Source: Ahrens, Jackson & Jackson (2012)

Gaseous Composition

Table 1.1 Composition of the Atmosphere Near Earth's Surface by Volume

PERMANENT GASES						
Gas	Symbol	Percent Dry Air by Volume	Parts per Million by Volume*	Atmospheric Sources (creation mechanisms)	Atmospheric Sinks (removal mechanisms)	Atmospheric Residence Time (years)
nitrogen	N_2	78.084	780,840	• decaying plants & animals • combustion	• nitrogen-fixing† soil bacteria • ocean plankton • lightning	14,000,000
oxygen	O_2	20.946	209,460	• photosynthesis • **photodissociation**‡ of water • photodissociation of nitrous oxide	• plant & animal respiration • decaying plants & animals • chemical rock weathering • growth of shellfish	4500
argon	Ar	0.93	9,300	radioactive decay of potassium	no sinks	forever, gradually accumulating
neon	Ne	0.0018	18	radioactive decay of rocks	no sinks	forever, gradually accumulating
helium	He	0.0005	5	radioactive decay of uranium & thorium	drifts into space	2,000,000
hydrogen	H_2	0.00006	0.6	• oxidation of methane • automobile exhaust • volcanoes	drifts into space	6.5
xenon	Xe	0.000009	0.09	radioactive decay of rocks	no sinks	forever, gradually accumulating

Source: Ahrens, Jackson & Jackson (2016)

Gaseous Composition – cont'd

Gas & Particles	Symbol	Percent Dry Air by Volume	Parts per Million by Volume*	Atmospheric Sources (creation mechanisms)	Atmospheric Sinks (removal mechanism)	Residence Time (years)
water vapour	H_2O	0 to 4	0 to 40,000	• evaporation • transpiration	precipitation	0.026 (9.5 days)
carbon dioxide	CO_2	0.0400	400§	• respiration • fire • oceans • fossil fuels & cement production • land-use change • freshwater outgassing • volcanoes	• photosynthesis • oceans	5 to 200 plus, depending on source
methane	CH_4	0.000182	1.82	• wetlands • fossil fuels • livestock's digestion • landfills & waste treatment • freshwater outgassing • biomass burning • soil outgassing • rice growing • termites • ocean bacteria	• atmospheric oxidation • uptake by soil bacteria	8.4

Source: Ahrens, Jackson & Jackson (2016)

Gaseous Composition – cont'd

VARIABLE GASES (*Continued*)

Gas & Particles	Symbol	Percent Dry Air by Volume	Parts per Million by Volume*	Atmospheric Sources (creation mechanisms)	Atmospheric Sinks (removal mechanism)	Atmospheric Residence Time (years)
nitrous oxide	N_2O	0.0000314	0.314	• nitrogen breakdown by bacteria in soils & oceans • agricultural soils & manure • fossil fuels • sewage	• chemical reactions in the stratosphere • uptake by soils	120
ozone	O_3	0.000004	0.04‖	• photodissociation of O_2 • photochemical smog	• chemical reaction: forms O_2 in stratosphere • reacts with vegetation	0.25 (91 days)
particles (dust, soot, etc.)		0.000001	0.01–0.15	• volcanoes • soil dust • fires • sea spray • fossil fuel burning	• washout by rain • settling by gravity	0 to 0.04 (minutes to 14 days, depending on size in the troposphere & longer in the stratosphere)
chlorofluo-rocarbons	CFCs	0.00000002	0.0002	manufactured: refrigerants, pro-pellants, & solvents	photodissociation‡	55 (for CFC11); 140 (for CFC12

*Parts per million (ppm) by volume measures very small amounts; for example, 5 ppm of ozone means there are five O_3 molecules in every 1,000,000 air molecules.

†Soil bacteria convert atmospheric nitrogen (N_2) to ammonia (NH_3), a form accessible to plants and other organisms.

‡The breakdown of compounds by ultraviolet radiation in the stratosphere (at altitudes between 11 and 50 km).

§Data change annually; values are as of 2015.

‖Surface ozone concentration is very small in comparison to O_3 in the stratosphere (at altitudes between 11 and 50 km) where values are ~5 to 12 ppm.

Source: Ahrens, Jackson & Jackson (2016)

The polluted atmosphere

- **Air pollution** is the introduction into the atmosphere of gases or aerosols (AKA liquid or solid particulate matter) from natural or anthropogenic (human) sources that cause harm or discomfort to humans or other living organisms, or cause damage to the natural environment or built environment.
- Air pollution in an indoor and outdoor (ambient) issue – in this course we will mainly discuss outdoor air quality

Types of air pollution

- Primary (emitted directly) / Secondary (forms in the atmosphere)
- Gaseous / Aerosol (particulate)
- Natural / Human-generated
- Hazardous AP (HAPs - toxics) / Criteria Air Contaminants (CACs)
- Source configuration:
  - Mobile / Stationary
    - Point
    - Line
    - Area

Table 18.1 Some of the Sources of Primary Air Pollutants

	SOURCES	POLLUTANTS
Natural	volcanic eruptions	particles (dust, ash), gases (SO_2, CO_2)
	forest fires	smoke, unburned hydrocarbons, CO_2, nitrogen oxides, ash
	dust storms	suspended particulate matter
	ocean waves	salt particles
	vegetation	hydrocarbons (VOCs),* pollens
	hot springs	sulphurous gases
Human caused		
Industrial	pulp and paper mills	particulate matter, sulphur oxides, reduced sulphur
	coal-fired power plants	ash, sulphur oxides, nitrogen oxides
	oil-burning power plants	sulphur oxides, nitrogen oxides, CO
	refineries	hydrocarbons, sulphur oxides, CO
	sulphuric acid manufacture	SO_2, SO_3, and H_2SO_4
	phosphate fertilizer manufacture	particulate matter, gaseous fluoride
	iron and steel mills	NO_X, SO_X, VOC, particulate matter, CO, metal oxides, smoke, fumes, dust, organic and inorganic gases
	base metal smelting	SO_2, particulate matter, heavy metals, dioxins
	manufacturing plastics	gaseous resin
	varnish/paint plants	acrolein, sulphur compounds
	automobiles, trucks, lawn and garden equipment, etc.	CO, nitrogen oxides, hydrocarbons (VOCs), particulate matter
Personal	home furnaces/fireplaces	CO, particulate matter
	open burning of refuse	CO, particulate matter

*VOCs are volatile organic compounds; they represent a class of organic compounds, most of which are hydrocarbons.

Some sources of primary air pollutants

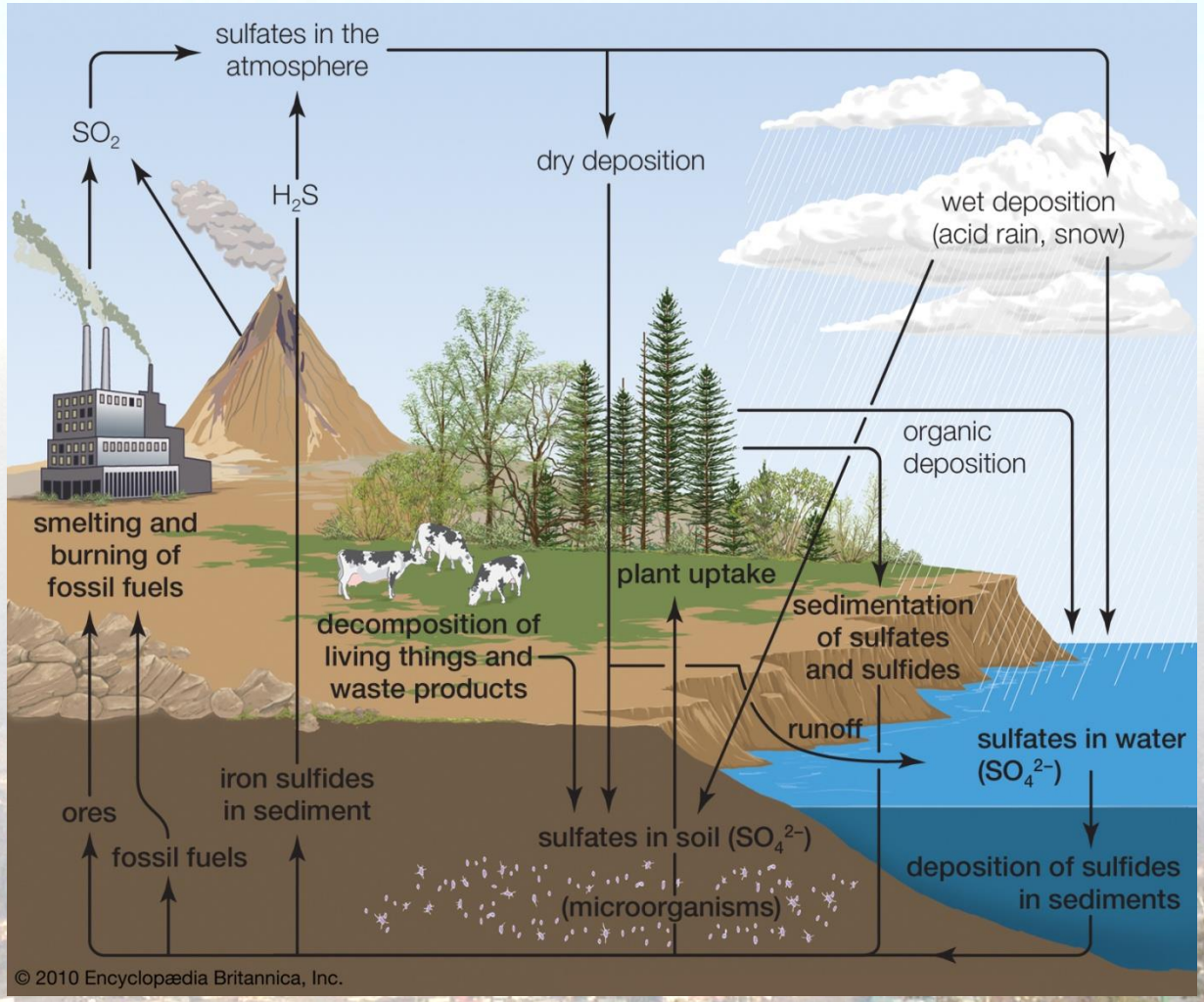
Source: Ahrens, Jackson & Jackson (2016)

Gaseous Pollutants

Gaseous pollutants can be categorized into 6 broad classes:

1. Sulphur containing compounds. carbonyl sulphide (COS); carbon disulphide (CS_2), dimethly sulphide ($(CH_3)_2S$), hydrogen sulphide (H_2S), sulphur dioxide (SO_2), and sulphate (SO_4^{2-}). Sources are biological decay, combustion of fossil fuels and organic matter, sea spray.

Sulphur cycle

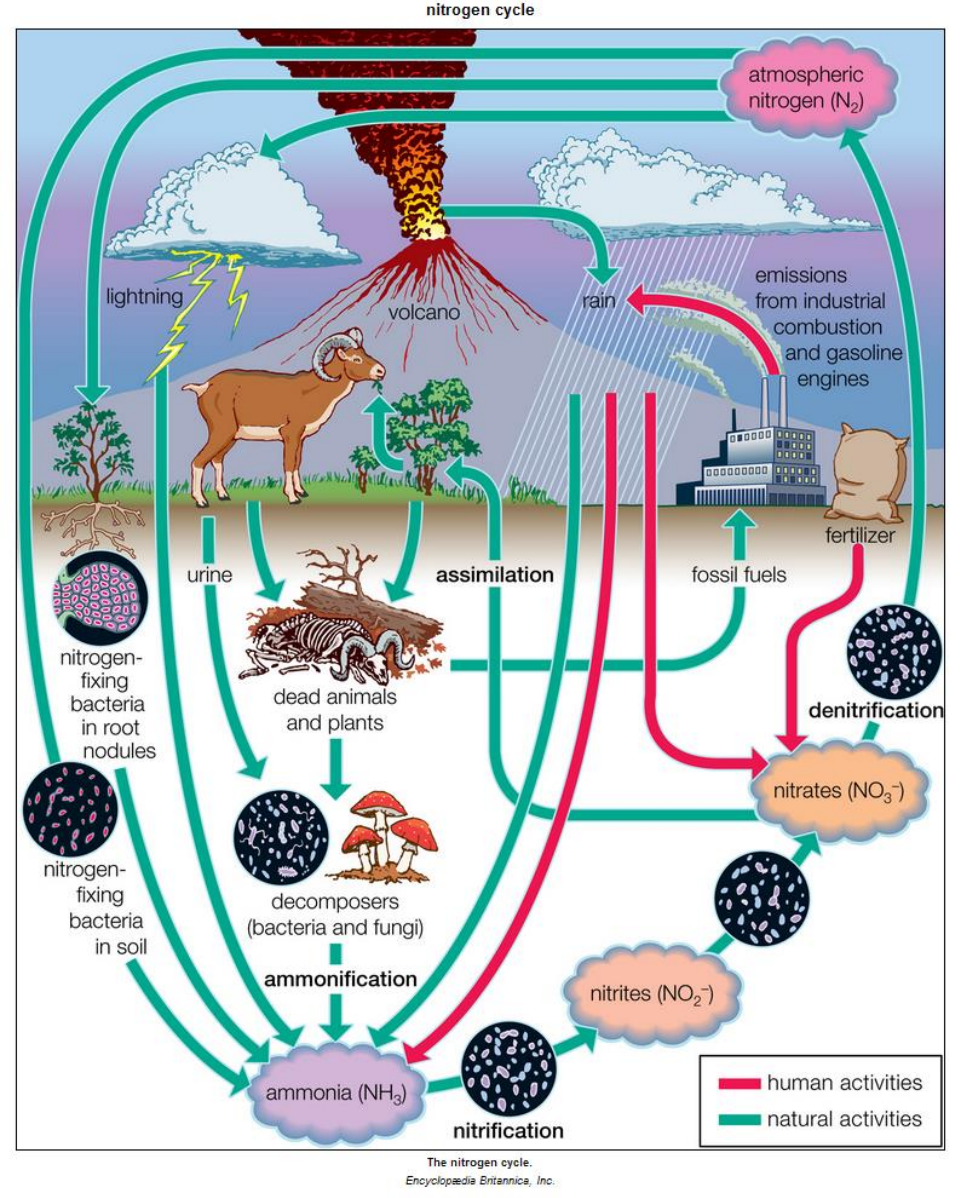


- Source: http://www.britannica.com/bps/media-view/111671/1/0/0

Gaseous Pollutants – cont'd

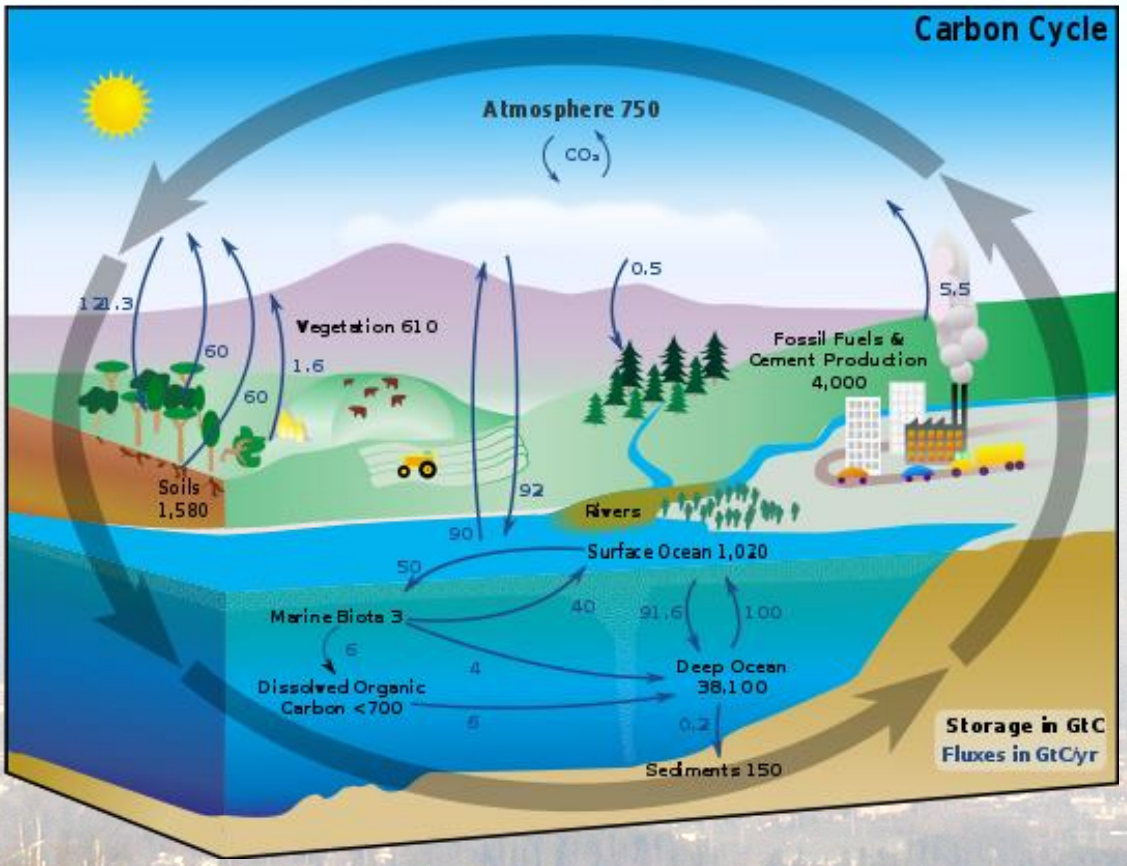
2. Nitrogen containing compounds. N_2O (nitrous oxide or laughing gas, inert in troposphere, emitted by natural bacterial action in soils), NO (nitric oxide emitted by natural and high temperature burning sources), NO_2 (nitrogen dioxide is emitted in small quantities by burning, but primarily formed by oxidation of NO), NH_3 (ammonia primarily natural) , and salts of NO_3^-, NO_2^-, and NH_4^+ (not emitted in significant quantities but result from conversion of NO, NO_2, and NH_3).

Nitrogen Cycle



- Source: http://www.britannica.com/bps/media-view/6/1/0/0

Gaseous Pollutants – cont'd



3. Carbon containing compounds of which hydrocarbons are a major group. There are many of these emitted from both natural and anthropogenic sources.

Source: http://en.wikipedia.org/wiki/File:Carbon_cycle-cute_diagram.svg

Gaseous Pollutants – cont'd

4. Halogen containing compounds. These are carbon compounds with halogens attached (usually Cl, but also Br, I). Are important because of contributions of CFCs to stratospheric ozone depletion, HCl to acid precipitation.

Gaseous Pollutants – cont'd

5. Toxic substances (may include pollutants from other classes) are usually so classified because they are carcinogenic. Arsenic (by-product of metal refining and used in pesticide, glass, and pharmaceutical manufacturing), Asbestos (many uses), Benzene (component of gasoline and used as a solvent), Cadmium (electroplating, plastics, pigments, batteries, etc), Carbon Tetrachloride (CCl_4 used in fluorocarbon production, etc), Chloroform ($CHCl_3$ used as a refrigerant and propellant, and as a resin), Chromium (used in steel production, chemical production), 1,4-Dioxane (stabilizer in solvents), …

Gaseous Pollutants – cont'd

5. Cont'd. Ethylene Dibromide ($C_2H_4Br_2$used in leaded gasoline, soil and seed fumigant, dye and pharmaceutical manufacture, solvent), Ethylene Dichloride ($C_2H_4Cl_2$ is heavily used in vinyl chloride production, and in production of other chemicals, solvent, lead scavenger in gasoline, adhesives, fumigants, paint remover, etc), Inorganic Lead (vehicle exhaust), Nickel (manufacture of chemicals, appliances, machinery, petroleum etc), Nitrosamines (rubber processing, organic chemical manufacture, rocket fuel), Perchloroethylene (C_2Cl_4 solvent used in dry cleaning, fabric finishing, degreasing), Polycyclic Aromatic Hydrocarbons (PAH emitted from coal burning, residential furnaces, coke production, wood and other burning), Vinyl Chloride (parent chemical of PVC).
6. Radioactive compounds (not considered here)

Aerosols (Particulate Matter - PM)

- Gases and vapours are individual molecules in random motion, exerting a partial pressure.
- Particles are aggregates of many molecules which can react with gases, act as condensation nuclei for vapour, etc.
- Larger particles are more likely to fall out of the air quickly by sedimentation.
- Small particles (between about .1 and 10 μm in diameter) can remain suspended until washed out of the air by precipitation, impaction on surfaces, agglomeration with other particles (which then become large enough to sediment out).

PM – cont'd

- There are several natural sources of particles in the system:
  - salt from evaporation of sea spray
  - pollen, fungi, molds, algae, yeasts, rusts, bacteria
  - debris from plants and animals
  - particles eroded by the wind
  - volcanic eruption, forest fires

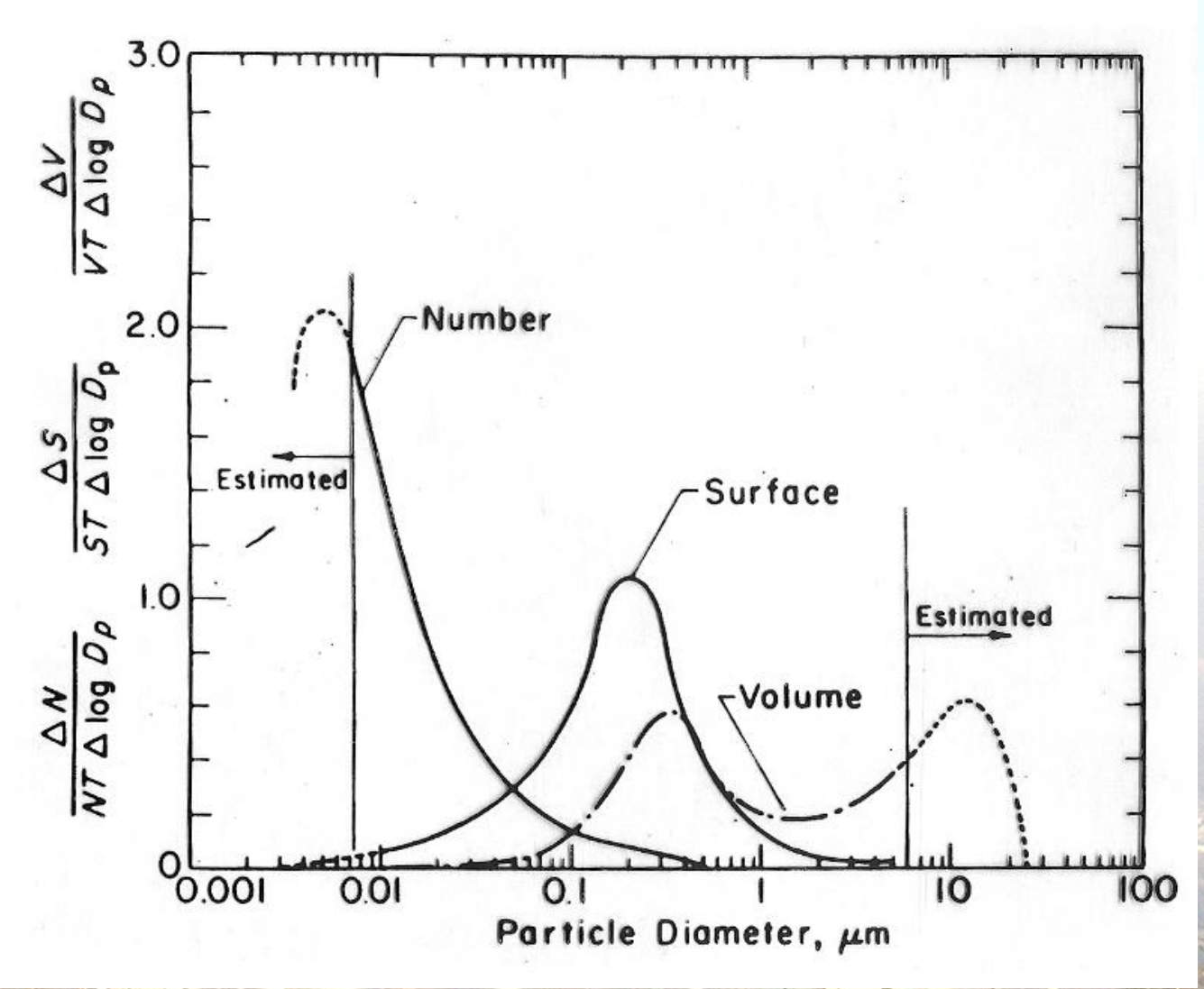
PM – cont'd

- Particle size is measured in microns ($\mu m = 10^{-6} m$).
- One particulate measure is TSP - total suspended particulates.
- Recently however more concern is given to PM_{10} and $PM_{2.5}$ (particles with diameters less than 10 and 2.5 μm).
- Particulate amount is usually measured as a mass density, but can also be measured as a number density.
- It is very difficult to measure the smallest suspended particles gravimetrically since they are so much less massive than the larger suspended particles. (e.g. a 0.1μm diameter particle is one millionth the mass of a 10 μm diameter particle).

Particulate Matter – What is it?

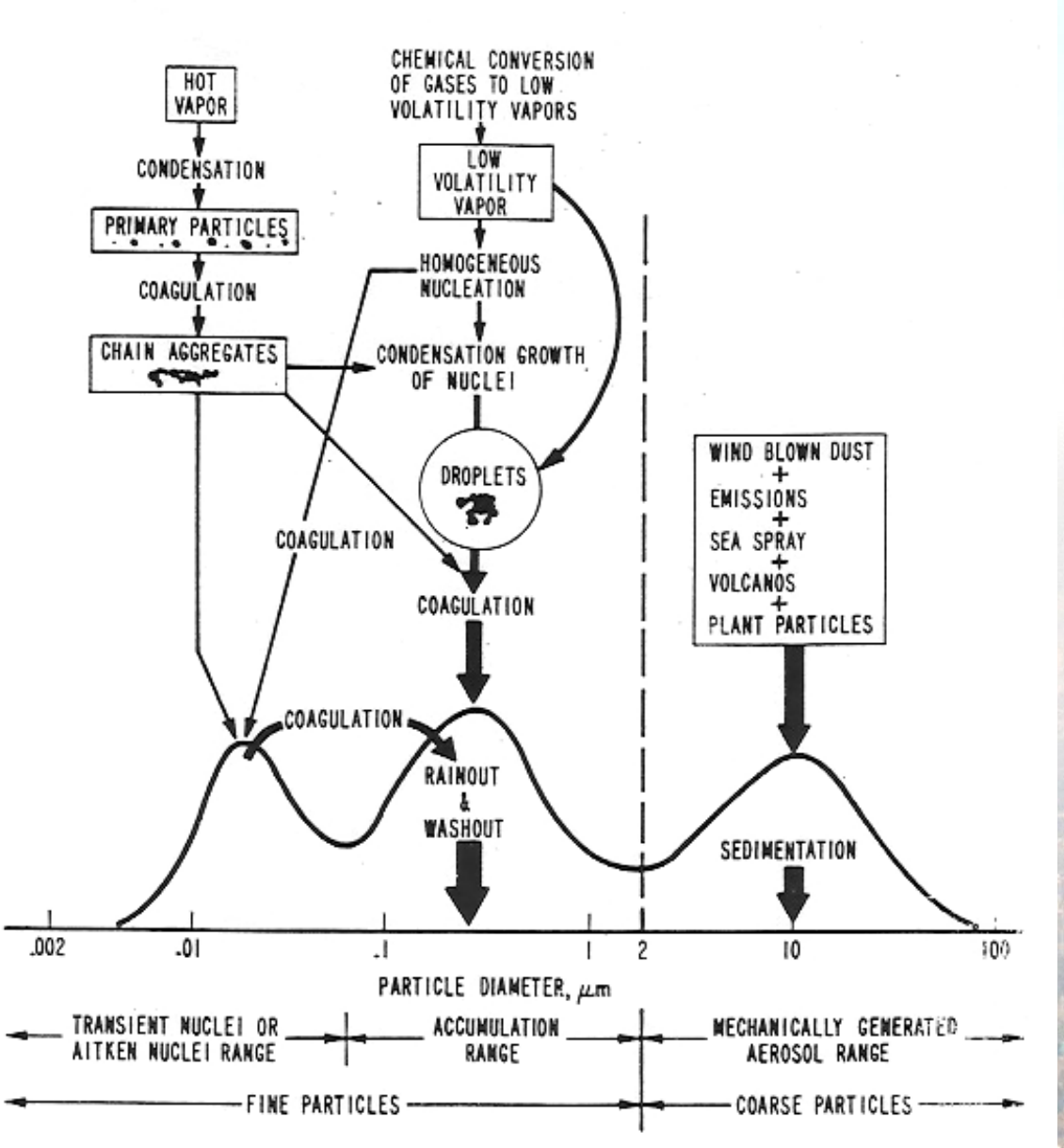
- PM_{10} - a particle of 10 microns, about 1/5th the width of a human hair.
- $PM_{2.5}$ - a particle of 2.5 microns, about 1/20th the width of a human hair
- BC Ministry of Health has called PM **"single greatest air pollution problem in BC"**
- PM_{10} – travels into the lungs and cause a variety of respiratory problems
- $PM_{2.5}$- penetrates the respiratory system deeper and is therefore more of a problem than the sizes > 2.5 microns

PM – cont'd



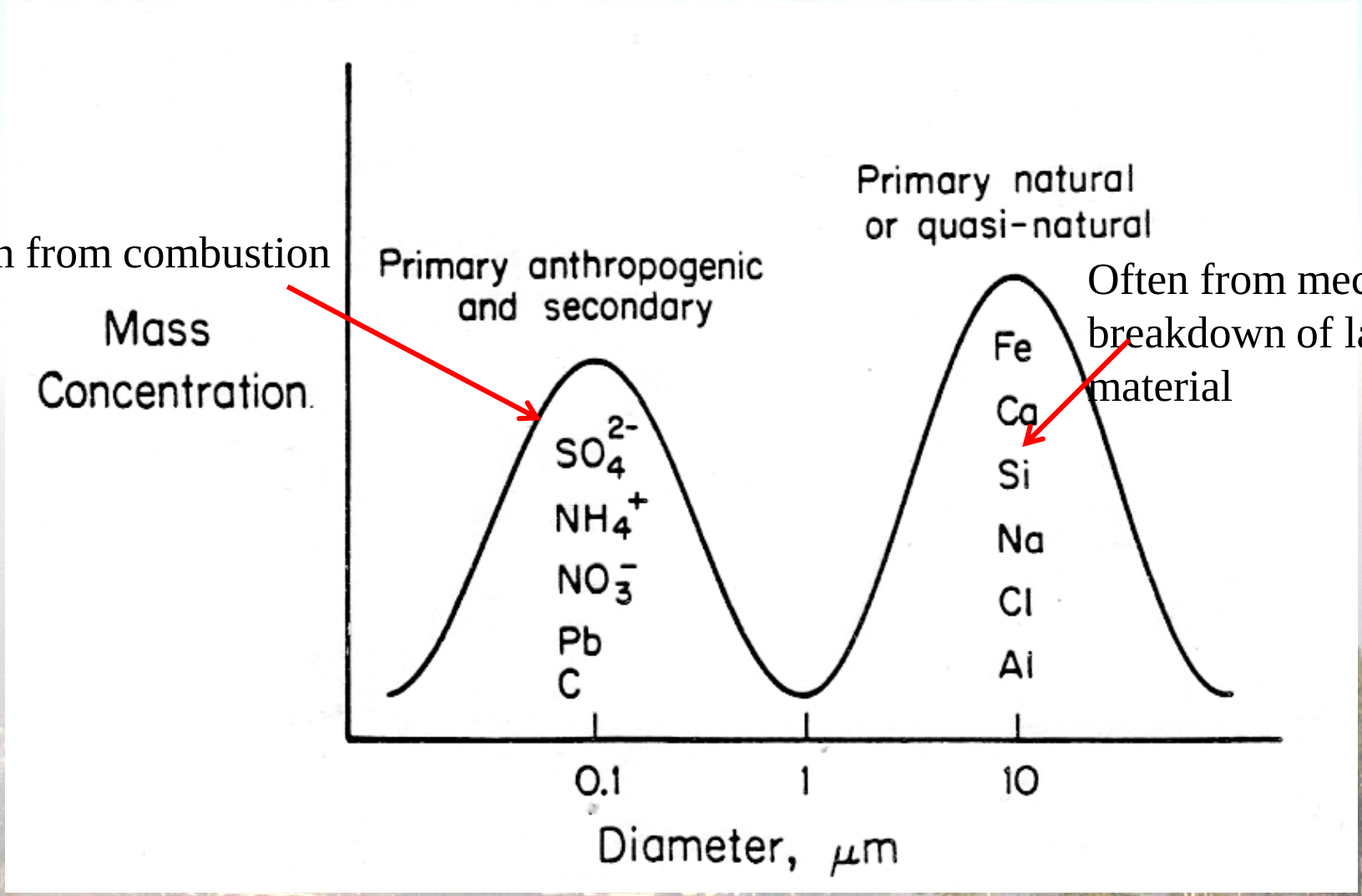
- Fig 2-3: Number (N), surface area (S), and volume (V) distribution of LA Smog normalized by total number (NT), area (ST) or volume (VT). Source: Corn, M. Properties of non-viable particles in the air, In "Air Pollution" 3rd ed. (A.C. Stern, ed.), 1976, p. 123.

PM – cont'd



- Fig. 1.5: Idealized schematic of the distribution of particle surface area of an aerosol (Whitby and Cantrell, 1976) indicating the modes, sources and particle formation and removal mechanisms. Source: Seinfeld (1986)

PM – cont'd

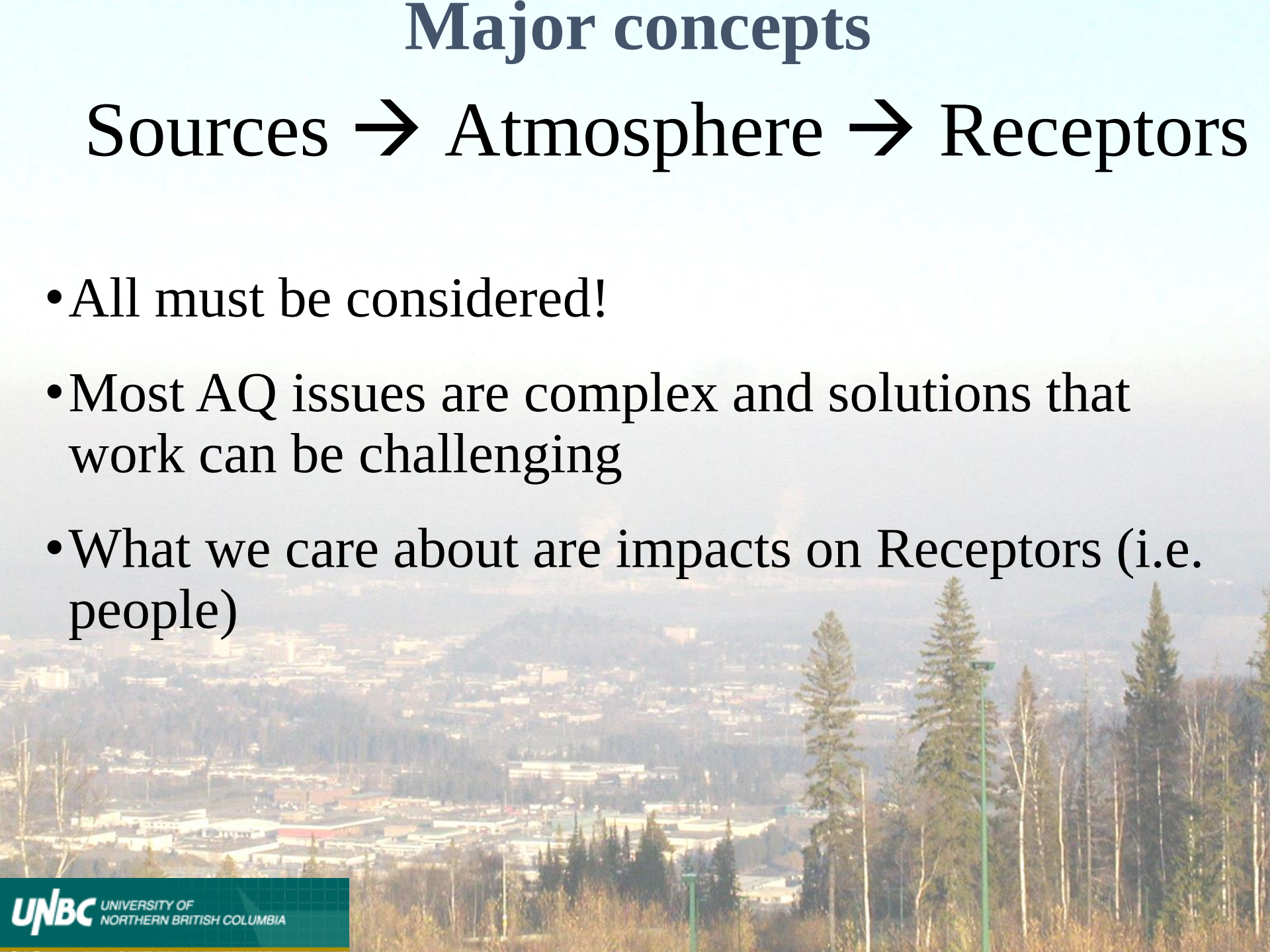


- Fig. 1.6: Idealized aerosol mass distribution showing typical segmentation of chemical species into fine and coarse particle fractions.Source: Seinfeld (1986).

Major concepts

Sources → Atmosphere → Receptors

- All must be considered!
- Most AQ issues are complex and solutions that work can be challenging
- What we care about are impacts on Receptors (i.e. people)



Sources

- No source = no pollution!
- Amount, configuration, characteristics all important
- Total discharge of a particular source may not be as important as other factors (e.g. elevation of emission, distance from population)

Sources – cont'd

- Sources are where pollutants are emitted, sinks are where they are removed.
- There are significant natural sources (e.g. respiration of plants and animals, decay of living matter, volcanos, forest fires).
- Sources can be both mobile and stationary.

Sinks

- Sinks include vegetation, soil, water, structures
- Pollutants are removed by *scavenging mechanisms*.
- Removal rate of a pollutants is given by its half life, which for most pollutants is on the order of days. This accounts for the fact that for most things, the composition of the atmosphere is not changing.

Sinks – cont'd

- Some pollutants accumulate such as CO_2, nitrous oxide (N_2O), methane (CH_4), CFCs etc, which have a long half life.

- oxidation (ie. reaction with oxygen), is an important removal mechanism for organic and inorganic gases.

- Inorganic gases (NO, NO_2, H_2S, SO_2, SO_3 can oxidize to eventually form acid gases.

Receptors

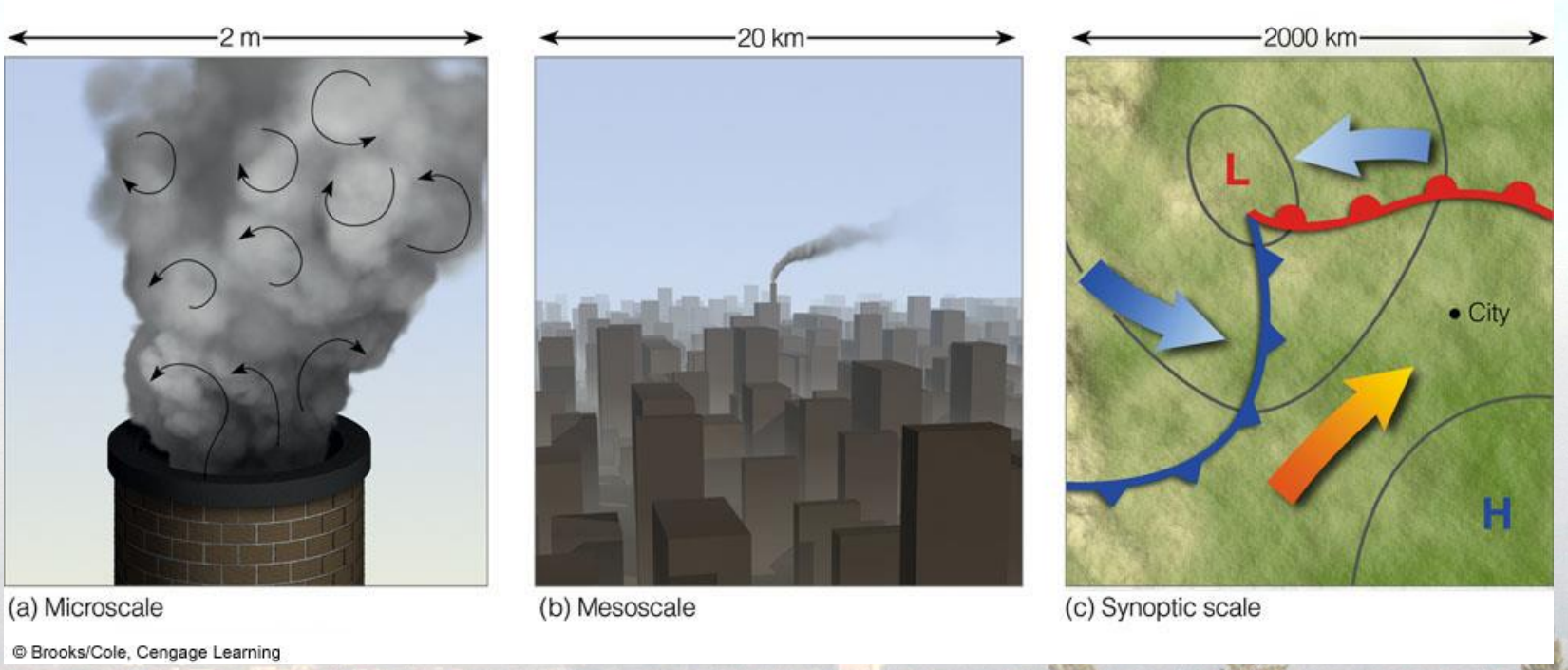
- Something which is negatively affected by pollution. Can be
  - animal / human whose health is affected (lungs / heart, eyes, skin)
  - vegetation death or damage
  - material damaged
  - atmosphere affected (eg. changed absorptivity)
  - soils damaged, lakes damaged (acid rain)

Transport and diffusion

- Wind both *transports* a pollutant from its source to a receptor, and *diffuses* the concentration of the pollutant due to turbulence, meandering and stretching as the plume advects downwind.

- Pollutant plumes above the Planetary Boundary Layer (PBL) may travel long distances before coming down to earth (Long-range transport of atmospheric pollutants – LRTAP)

Scales of Air Pollution



Air pollution exists at all scales. At the microscale, mixing and diffusion occurs.

Local / urban (mesoscale)

- usually characterized by either a few large emitters or by many small emitters
- lower release heights have a larger impact since pollutants are released into a lower wind speed environment away from the diffusive characteristics of the free atmosphere, and are closer to most receptors of interest.
- at the local scale, the details of roughness elements can become important in how the atmosphere transports and disperses pollutants, and hence the ambient concentration.

Local / urban (mesoscale) – cont'd

- slowly reacting pollutants (e.g. CO, PM, SO_2) emissions from multiple sources can add together in certain areas resulting in high concentrations (eg. at an intersection in an urban canyon).
- ozone is a secondary pollutant formed when oxides of nitrogen react with hydrocarbons in the presence of sunlight. It is a serious problem in many larger urban areas.

Regional – continental scale

- propagation downwind of a polluted urban plume which affects the region

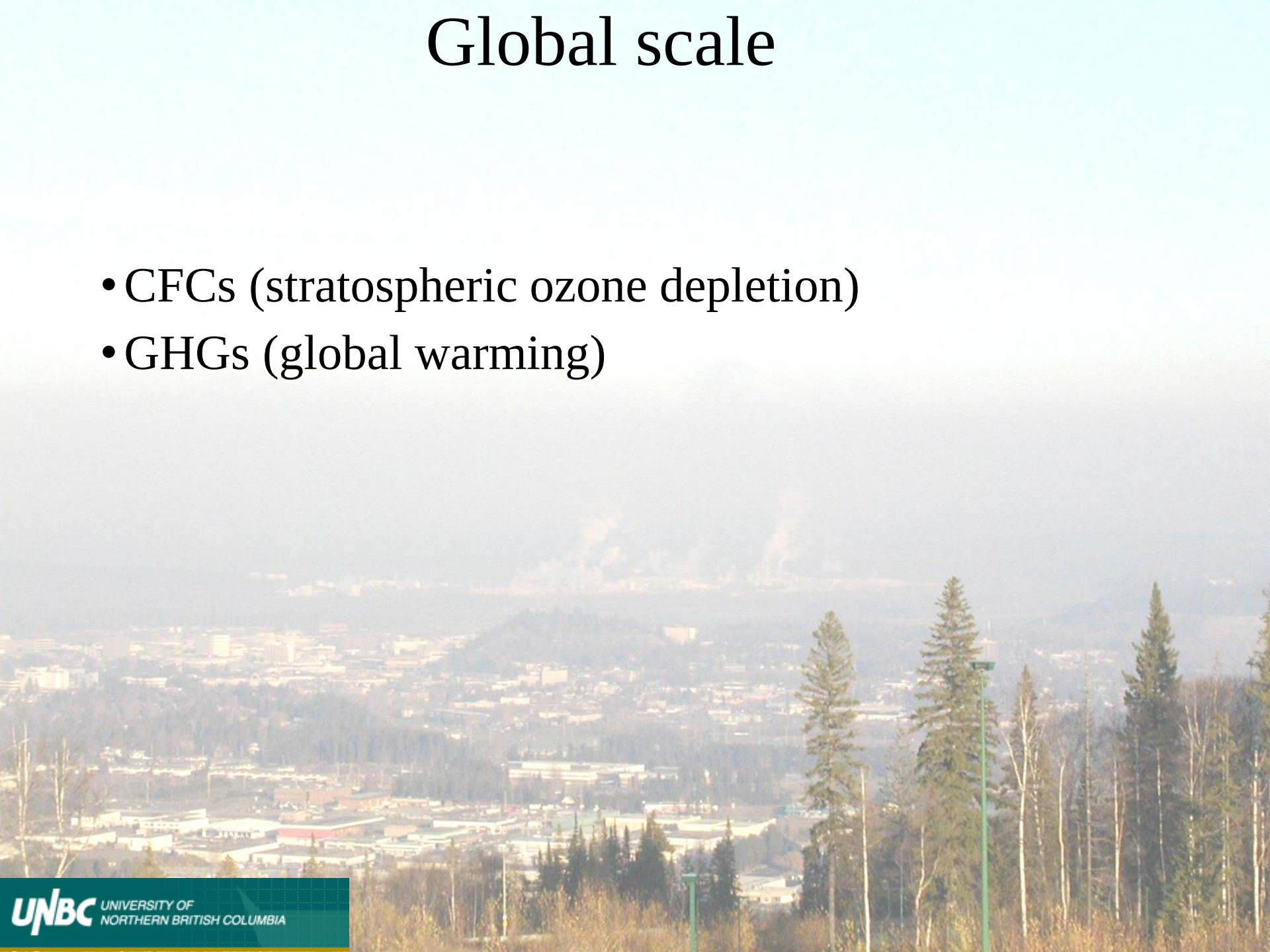
- release of relatively slow reacting primary pollutants that undergo transformations during long transport times. e.g. ``acid rain'' which occurs when either SO_2, released from combustion, gets oxidized to SO_3 which reacts with water vapour to form H_2SO_4 which form sulphate particulates; or

- NO resulting from high temperature combustion is oxidized to NO_2 which reacts to form nitrate particles. The sulphate and nitrate particles ($< 1\mu m$) can act as CCN resulting in acid rain.

- visibility can be reduced regionally (especially by sulphate and nitrate particles)

Global scale

- CFCs (stratospheric ozone depletion)
- GHGs (global warming)



Readings for next week

- Text: Chapters 4, 6, 22
- Gaffney and Marley (2009). Combustion.