JIMMA UNIVERSITY
COLLEGE OF NATURAL SCIENCE
DEPARTMENT OF CHEMISTRY

❑ Environmental chemistry and Toxicology **(Chem 3114).**

➢ Course to be offered; to Chemistry BSc students

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Course out line

- ❑Chapter 1: Introduction to environmental chemistry
- ❑Chapter 2: Aquatic and water chemistry
- ❑Chapter 3: Atmospheric chemistry and Air
- ❑Chapter 4: Soil chemistry
- ❑Chapter 5: Environmental Toxicity and toxicology
- ❑Chapter 6: Green chemistry

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Assessments

- ❖Continuous assessment
- ✓Quiz and assignment
- ✓Mid exam
- ✓Field trip report and presentation
- ❖Final exams

Cont.,

- **Environmental science**
  - is defined as the study of the earth, air, water, and the living environments, and the effects of technology there on.
- **Environment**
  - The place where we live or work?
  - The atmosphere which we breathe and water which we drink?
  - ✓ consists of the biosphere, the atmosphere, the geosphere, the hydrosphere, the anthroposphere, and all the fauna and flora, with their interactions as a whole.

Ecology and Ecosystem

- ***Ecology*** is the science that deals with the relationships between living organisms with their physical environment & with each other.

- ***An ecosystem*** consists of an assembly of mutually interacting organisms and their environment in which materials are interchanged in a largely cyclical manner.

- An ecosystem has physical chemical & biological components along with energy sources & pathways of energy & materials interchange.

Cont.,

❑ ***Dividing Ecology it into four categories***

1. Terrestrial environment
2. Freshwater environment
3. Oceanic marine environment
4. Symbiotic environment

Both – sided Impacts

❖ **Impact of Man upon the Environment**

- Humans alone have the ability to gather resources from beyond their immediate surroundings and process those resources into different, more versatile forms
- human population to thrive and furnish beyond natural constraints.
- But the natural and manufactured wastes generated and released into the biosphere
- *Anthropogenic* (human induced) pollutants have overloaded the system.

Both – sided Impacts---cont’d

❖ Impact of the Environment upon Man

- Elements of the air, the water, and the land may host harmful biological and chemical agents that impact the health of humans.

- A wide range of communicable diseases can be spread.
- Would affect the well-being of living organisms, whether it is physical (e.g. global warming), chemical (e.g. ozone layer depletion) or biological (e.g. destruction of rain forests).

Some definitions pertaining to pollution

- **Pollutant** is a substance present in greater than natural concentration as a result of human activity that has a net detrimental effect upon something of value in that environment.
- **Contaminants**, which are not classified as pollutants unless they have some detrimental effect, cause deviations from the normal composition of an environment.
- Every pollutant originates from a **source**.
- The source is particularly important because it is generally the logical place to eliminate pollution. Source of pollutants can be **point source or non-point** source.

Some definitions pertaining to pollution---cont’d

❖Pollution

- Means the **introduction by man, directly or indirectly**, of substances or energy into the environment **resulting in deleterious effects** of such a nature as to endanger human health, harm living resources or interfere with amenities or other legitimate use of the environment.

Environmental Chemistry

Definition

❖ **Environmental Chemistry is:**

➢ the study of the **sources, reactions, transport, effects, and fates of the chemical species** in the:

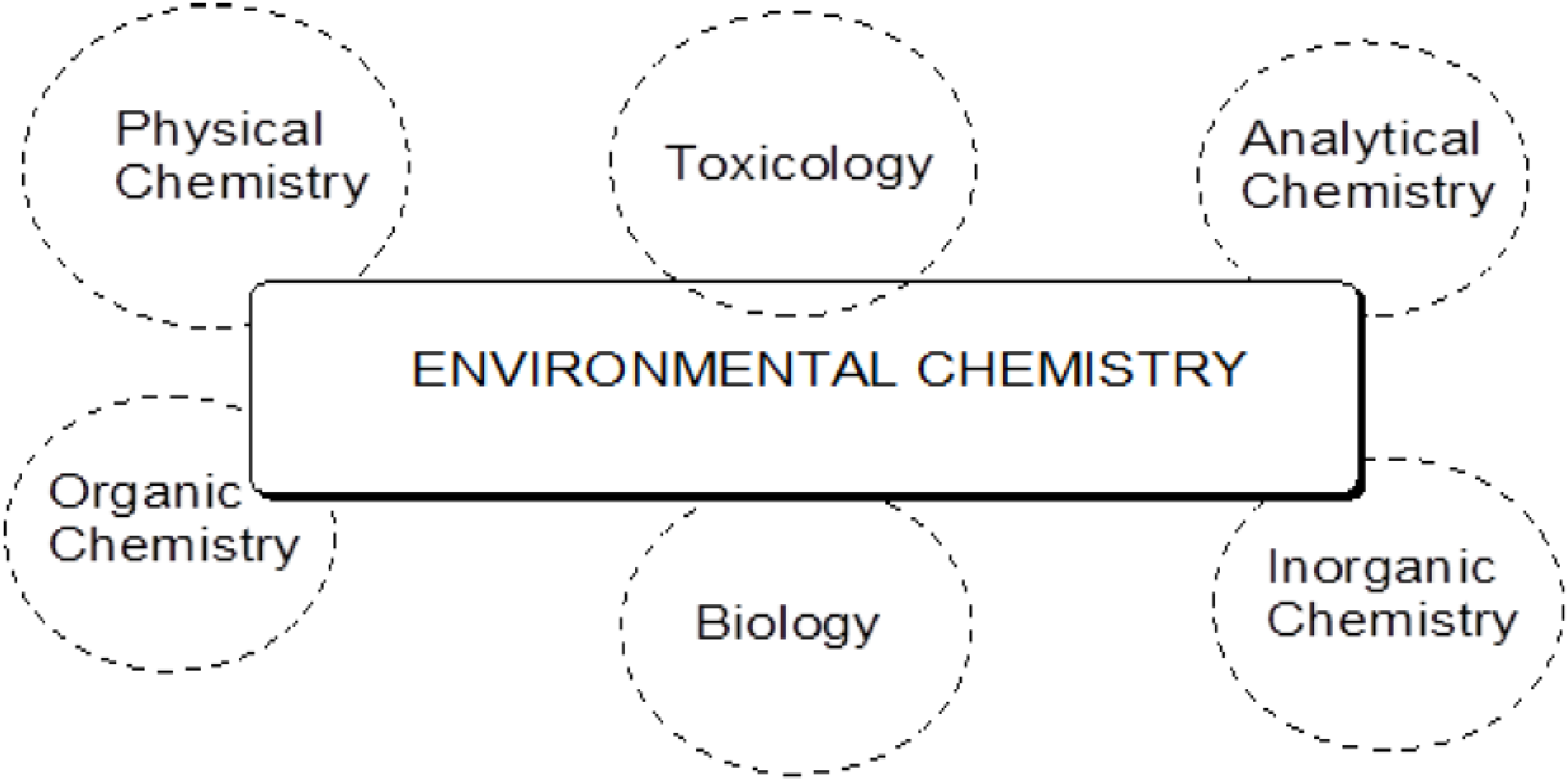
- ✓ **Air(Atmosphere),**
- ✓ **Soil(Geosphere),**
- ✓ **Water(Hydrosphere),**
- ✓ **Living environments(Biosphere),**
- ✓ **and the effects of technology(Antroposphere) thereon.**

Environmental Chemistry---cont’d

❖ Environmental chemistry is concerned with:

- The management of chemicals discharged to the env’t
- Pollution & the behavior of natural chemicals in the natural systems
- Developing an understanding of the chemistry of the world

Interdisciplinary



ENVIRONMENTAL CHEMISTRY

Physical Chemistry

Toxicology

Analytical Chemistry

Organic Chemistry

Biology

Inorganic Chemistry

1. Basic Concepts in Environmental chemistry

- The survival of humans relied on accurate interpretation of the surrounding environment gained by experience and observation.
- Nowadays, sophisticated instruments allow observations and provide knowledge about every aspect of human activities — including our future on this planet.
- Environmental chemistry as a distinct discipline, however, is rather new and emerged only in the last decades of the 20th century.
- Environmental chemistry investigates the effects different elements, molecules or chemical products have on the environment and the species living within it

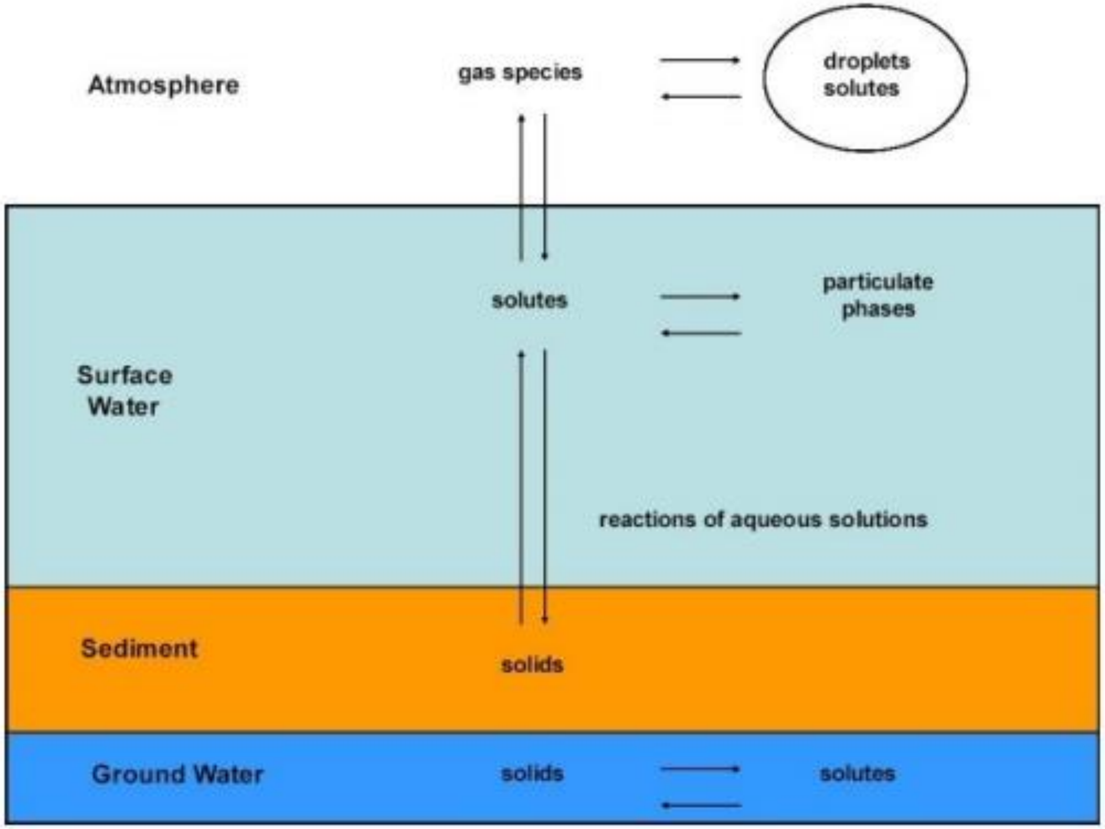
Cont,

- To consider the environmental chemist’s perspective. To understand the abundance and distribution as well as the transport, reactivity, and fate of pollutants and nutrients, it is useful to view the environment as divided into “compartments”.

- The four major pillars of the environment are
  - the biosphere (Living Things and *abiotic*),
  - the atmosphere (Air),
  - the hydrosphere (Water) : surface water; ground water; vapor, and
  - the geo-sphere or Lithosphere (Land); sediment soil

- Chemical reaction occur in each sphere separately and also differently. Examples: Global water cycle, Nutrient Cycle of carbon, nitrogen phosphorus etc.

Compartment



The geochemical make-up of the sediment is a source of iron and manganese oxides, upon reduction yielding relatively large amounts of dissolved Fe $^{2+}$ and Mn^{2+} to the surface water.

➢Processes that occur between these compartments are **a key area of interest to the environmental chemist**. Study of the movement and transformations occurring at these interfaces (e.g., air : water) is crucial in developing an understanding of transport and fate in particular.

Cont,

- **The primary structure of the atmosphere is four-fold:**
  - **the troposphere,**
  - **stratosphere,**
  - **mesosphere, and**
  - **thermosphere,**
- **Boundaries between these regions are known as :**
  - **the tropopause, stratopause, and mesopause, respectively.**
- **The main components of the hydrosphere are the oceans, where 97.61% of the water on Earth resides, polar ice and glaciers (2.08%), groundwater (0.30%), freshwater and saline lakes (each ~0.01%), with rivers, soil moisture, and atmospheric water vapor comprising the remainder.**

Cont.,

- All chemical species present in the environment are cycled among the different compartments.

- Examples the **hydrological cycle**

- During these cycling processes, chemical reactions convert species by reduction/oxidation, acid/base, precipitation, or complex formation and physical processes are responsible for phase changes, adsorption and partitioning.

- The time scale at which these different processes happen varies greatly

Processes in a compartment

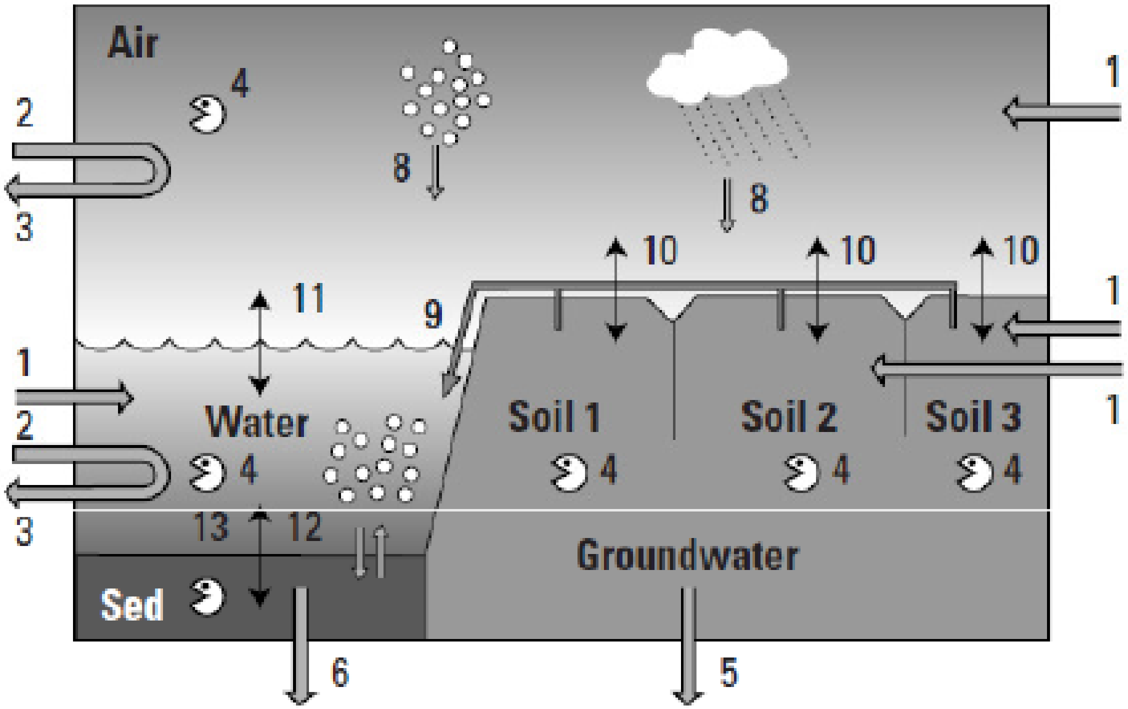


Figure 4.11. Diagram of a multimedia mass balance model concept. 1 = Emission, 2 = Import, 3 = Export, 4 = Degradation, 5 = Leaching, 6 = Burial, 7 = Wet deposition, 8 = Dry aerosol deposition, 9 = Run-off, 10, 11 = Gas absorption and volatilization, 12 = Sedimentation and resuspension, 13 = Sorption and desorption. From [61]

- Emission
- Equilibrium partitioning
- Intra-media transport
- Inter-media transport
- Abiotic transformation
- Biodegradation
- Bioconcentration
- Bioaccumulation
- Biomagnification

1.2. Properties of Chemicals in the Environment

- Do you know the properties of chemicals in the Environment?

1. List some of the chemicals found in the Environment ?
2. Explain the chemical and physical properties of substances in the Environment?

Behavior of chemicals in the environment

- is governed by their **physical** and **chemical** properties as well as **transformation** and **degradation** processes.
- understanding of these properties would be expected to give a clear perception of how compounds will behave in the environment.
- For example, compounds with low boiling points evaporate rapidly into the atmosphere, whereas compounds that are highly soluble in water disperse rapidly in streams and rivers.
- Properties of compounds are largely influenced by inter-molecular and intra-molecular forces.

Cont., these properties are Influenced by

- Physical States
- Polarity of bonds and molecules
- Boiling Point
- The melting point
- Density
- Solubility
- Partition Behavior
- Etc …

Equilibrium partitioning

- In systems that consist of more than one phase (i.e. most realistic systems), chemicals tend to migrate from one phase to another if the phases are not in equilibrium.

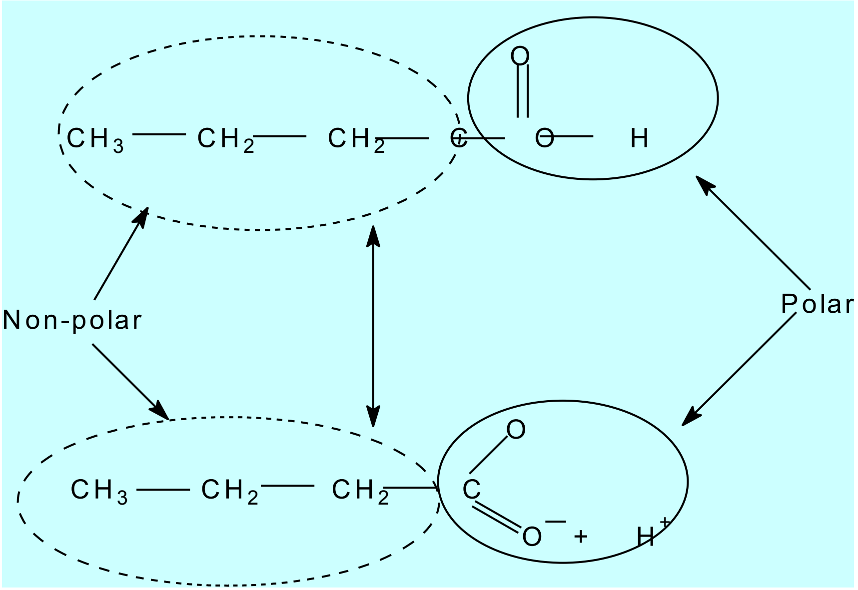
- the equilibrium between two phases is usually described with an equilibrium partition coefficient (K12), a ratio of the concentration in both phases (C1, C2) which is

$$K_{12} = \frac{C_1}{C_2}$$

Partition behavior;

$$K_{ow} = \frac{C_o}{C_w}$$

Butyric acid



partition coefficient of a given substance is **constant** ; in two specific liquids under constant environmental conditions such as **temperature and pressure**.

PARTITION COEFFICIENT

❑ The partition coefficient is dependent on:

- ➢ Polarity of the substance
- ➢ Molecular weight
- ➢ Relationship of the polarity of the solvent used.

Cont.,

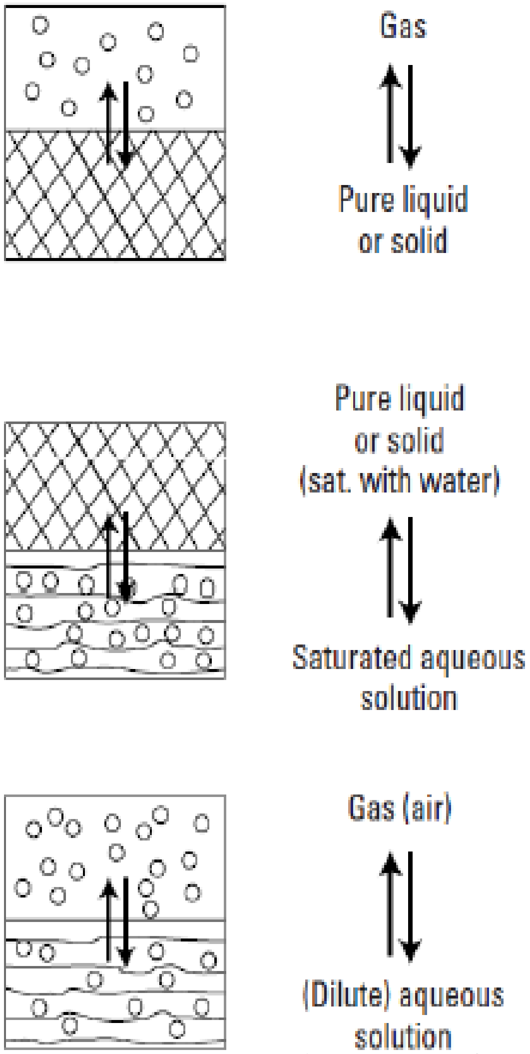
- Three partition coefficients are essential for exposure modeling of the environment:

✓**Air-water**(Kaw),

✓**Solid-water** (Kp or Kd) and

✓**Octanol-water** (Kow) partition coefficients

Equilibrium partitioning (air-water)



Compound property

Gas ⇅ Pure liquid or solid — Vapour pressure — P^s (Pa) (OECD 104)

Pure liquid or solid (sat. with water) ⇅ Saturated aqueous solution — Aqueous solubility — S (mol L^{-1}) (OECD 105)

$$H = \frac{P^S}{S}$$

Henry's Law Constant
(Pa m^3 mol^{-1})

Gas (air) ⇅ (Dilute) aqueous solution — Air-water partition constant (Henry constant) Air-water distribution ratio

Air-water Equilibirium Partition Constant (-):

$$K_{aw} = \frac{C_a}{C_w} = \frac{H}{R \cdot T}$$

C_a,C_w = concentration in air, water (mol L^{-1})
R = gas constant (8.314 Pa m^3 mol^{-1} K^{-1})
T = temperature at air-water interface (

Equilibrium partitioning (Octanol-water)

- One of the most widely used physico-chemical characteristics of compounds applied in environmental chemistry is:

the n-octanol/water partition coefficient.

- This partition coefficient is important because it imitates the biota lipid /water partition process.
- Octanol is in many ways similar to biota lipid since it is fat-like in many of its physical properties.
- The n-octanol/ water partition coefficient (Kow)

is defined as:

$$K_{ow} = \frac{C_o}{C_w}$$

C_o and C_w - are the concentration of the substance in octanol and in water

K_{ow}

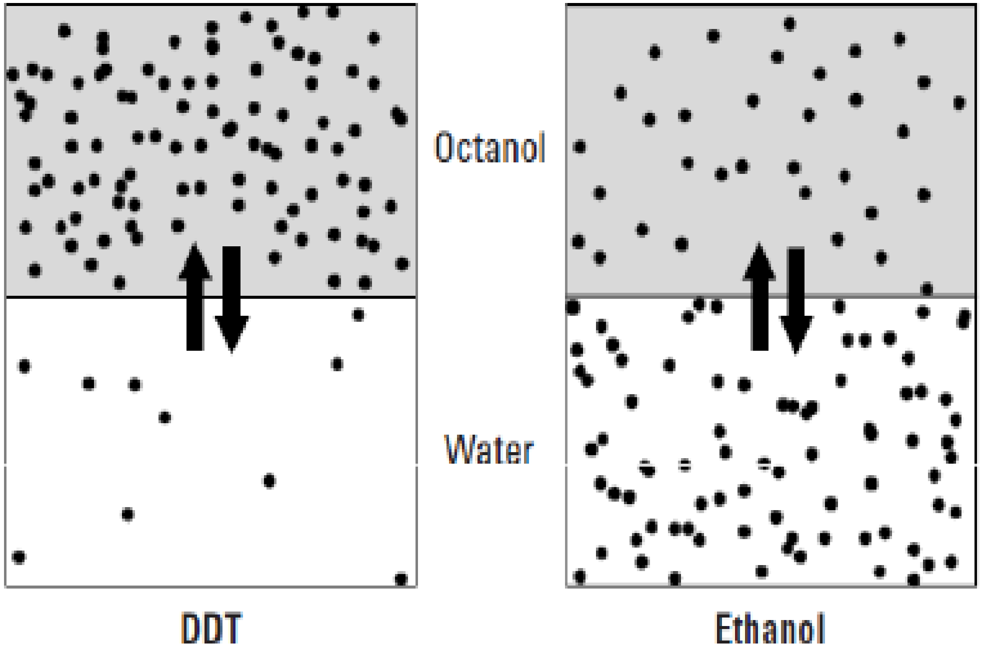


Figure 9.1. Illustrations of the octanol-water partition coefficient, together with examples of a hydrophobic (DDT = *p,p'*-dichlorodiphenyl trichloroethane) and a hydrophilic (ethanol) compound.

- Higher K_{ow} means:
  - More hydrophobic
  - More lipophilic
  - More lipid-soluble
  - Less hydrophilic
  - Lower water-solubility

Theoretical relation with water solubility:

$$\log_{10} S = -\log_{10} K_{ow} - 0.01 \cdot (MP - 25) + 0.5$$

MP= melting point (degrees Celsius)

Example Cont.,

- The Kow values are dimensionless since both Cw and Co are measured in the same units.
- ranges from about 0.001 to over 10,000,000.
- Some typical Kow values are:

Compound	Kow	Log Kow
Ethanol	0.49	-0.31
Benzene	134.90	2.13
2,4, - D	37.20	1.57
DDT	2.29×10^6	6.36

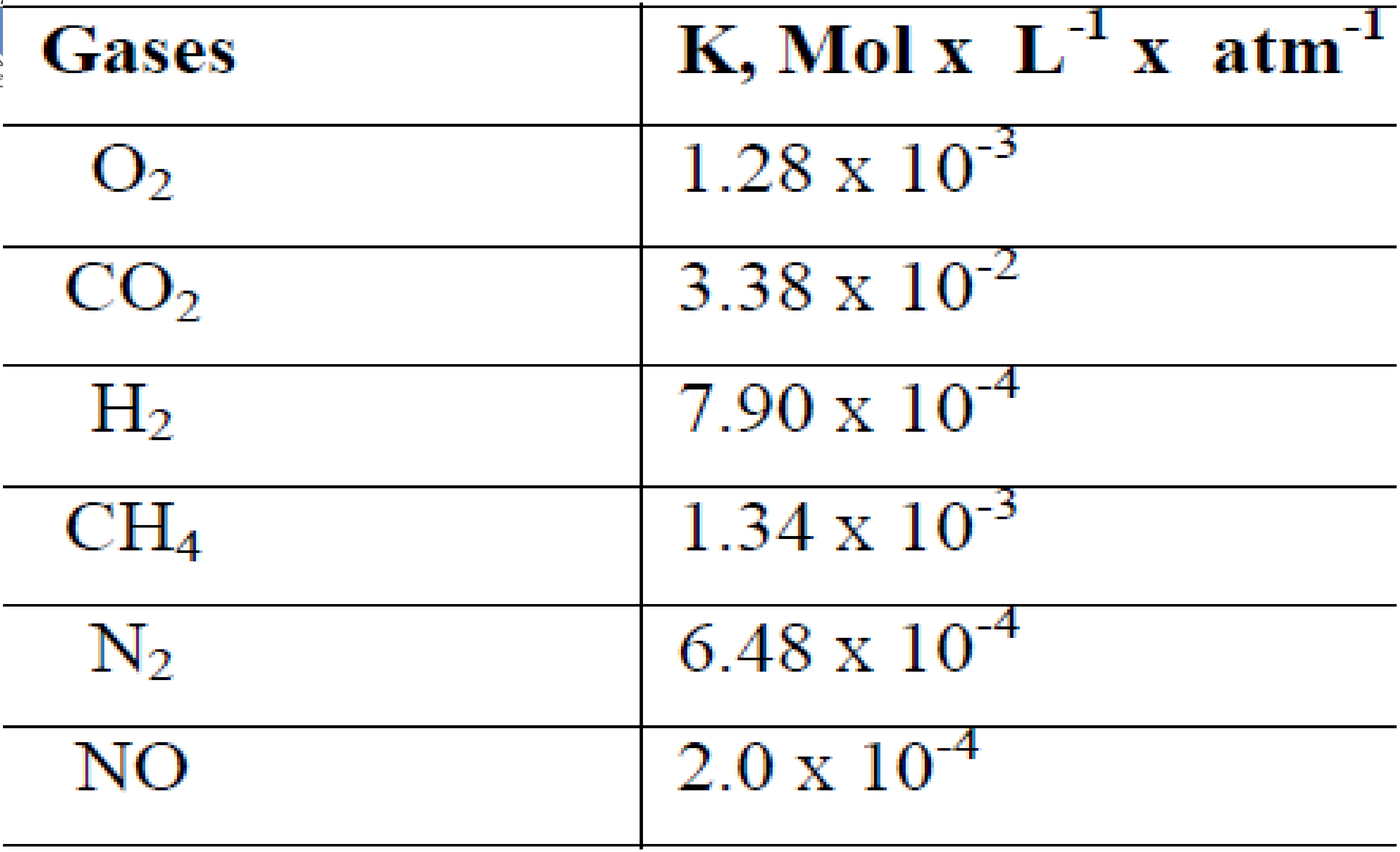
Solubility of gases

- The Solubility of gases in water is described by Henry‘s law, which states that —at constant temperature the solubility of a gas in liquid is proportional to the partial pressure of the gas in contact with the liquid‖.
- For a gas, X, this law applies to equilibrium of the type
- Henry‘s law constant (H) can also define as:

$$X(g) \rightleftharpoons X(aq) \qquad H = \frac{P}{C_w}$$

- Where P - partial pressure of the compound in air, Cw - is the corresponding concentration in water

Henry‘s law constants for some gases in water at 25^0C



Gases	K, Mol x L^{-1} x atm^{-1}
O_2	1.28×10^{-3}
CO_2	3.38×10^{-2}
H_2	7.90×10^{-4}
CH_4	1.34×10^{-3}
N_2	6.48×10^{-4}
NO	2.0×10^{-4}

Cont.,

- The Solubility of gases decrease with increasing temperature.
- Account is taken of this factor with the **Clausius -Clapeyron** equation

$$\mathrm{Log}\ {}^{C2}\!/\!_{C1} = \triangle\ {}^{H}\!/\!_{2.303R}\,[1/T_1-1/T_2]$$

- Where C1 and C2 denote the gas concentrations in water at absolute temperatures of T_1 and T_2, respectively; ΔH is the heat of solution; and R is the gas constant.
- The value of R is 1.987 cal x degree^{-1}xmol^{-1}, which gives ΔH in units of cal/mol.

Example

1. Considering that dry air is 20.95% by volume of oxygen, the partial pressure of water is 0.0313 atm; and the concentration of oxygen in water saturated with air at 1.00 atm. Based on the given data calculate the gas solubility of oxygen at 25^0C ?

Solution

- ☐ **$P_T = P_{gas} + P_{H2O}$**
- ☐ Where, P_{H2O} = Vapor pressure of H_2O from $P_{gas} = P_T - P_{H2O}$
- ☐ Therefore, $P_{O2} = P_T - P_{H2O}$
- ☐ P_{O2} = (1.0000 atm-0.0313atm) = 0.9687atm
- ☐ P_{O2} = (0.9687atm) x 0.2095 = 0.2029 atm

(since dry air is 20.95% by volume oxygen)

$[O2(aq)] = KxP_{O2}$

$= 1.28\times10^{-3} molL^{-1} \times atm^{-1} X\ 0.2029\ atm$

= 2.60 x 10-4 molL-1

$= 2.60 \times 10\text{-}4\ molL^{-1}\ X\ 32\ g/mol$

= **8.32mg/L, or 8.32ppm**

1.3. Environnemental Transformation and Dégradation processus

☐ **Transformation** and **degradation** may occur through interactions with other chemicals in the environment.

- By external environment or within the biota.
- input of energy in the form of radiation or heat.
- through biological processes.

Cont.,

- Generates a **daughter compound** with different physico-chemical and toxicological properties

❖ Depends on the **chemical's properties** (e.g., molecular structure)

❖ Depends on **environmental conditions**, such as:

✓-Temperature (all processes) (+)

✓- pH (~hydrolysis) (+/-)

✓- Light intensity (~photolysis) (+)

✓- Redox conditions, availability of electron acceptors/donors

✓(~oxidation/reduction) (+)

Biodegradation

- Transformation of chemicals by microorganisms (mainly bacteria) by means of their enzymatic machinery
- Primary degradation and mineralization
- Biodegradation plays a key role in the removal of chemicals from the aquatic and terrestrial environment
  - ✓ If too slow, the chemical may persist in the environment and ultimately accumulate in the food web (=bio magnification).
  - ✓ In aerobic environments, biodegradation is often equivalent to mineralization (complete conversion to inorganic end-products like water and CO2)
  - ✓ In anaerobic environments, biodegradation is usually slower and does usually not result in complete conversion

Reasons for biodegradability vs. persistence

❑ Chemical structure

➢ Aliphatic (+) vs. aromatic (-)

➢ Nature, type and number of substituents (-)

➢ Presence of ether groups (-)

❑ Environmental conditions and bioavailability

➢ Temperature (+)

➢ Inorganic nutrients (+)

➢ Organic Matter (-), Particles (-) (~bioavailability)

➢ Presence of other, similar pollutants (+)

➢ Presence and population density of specialized degraders (~acclimated and adapted populations) (+) = very decisive for biodegradation and very different among different ecosystems

Growth of pattern of a microbial population

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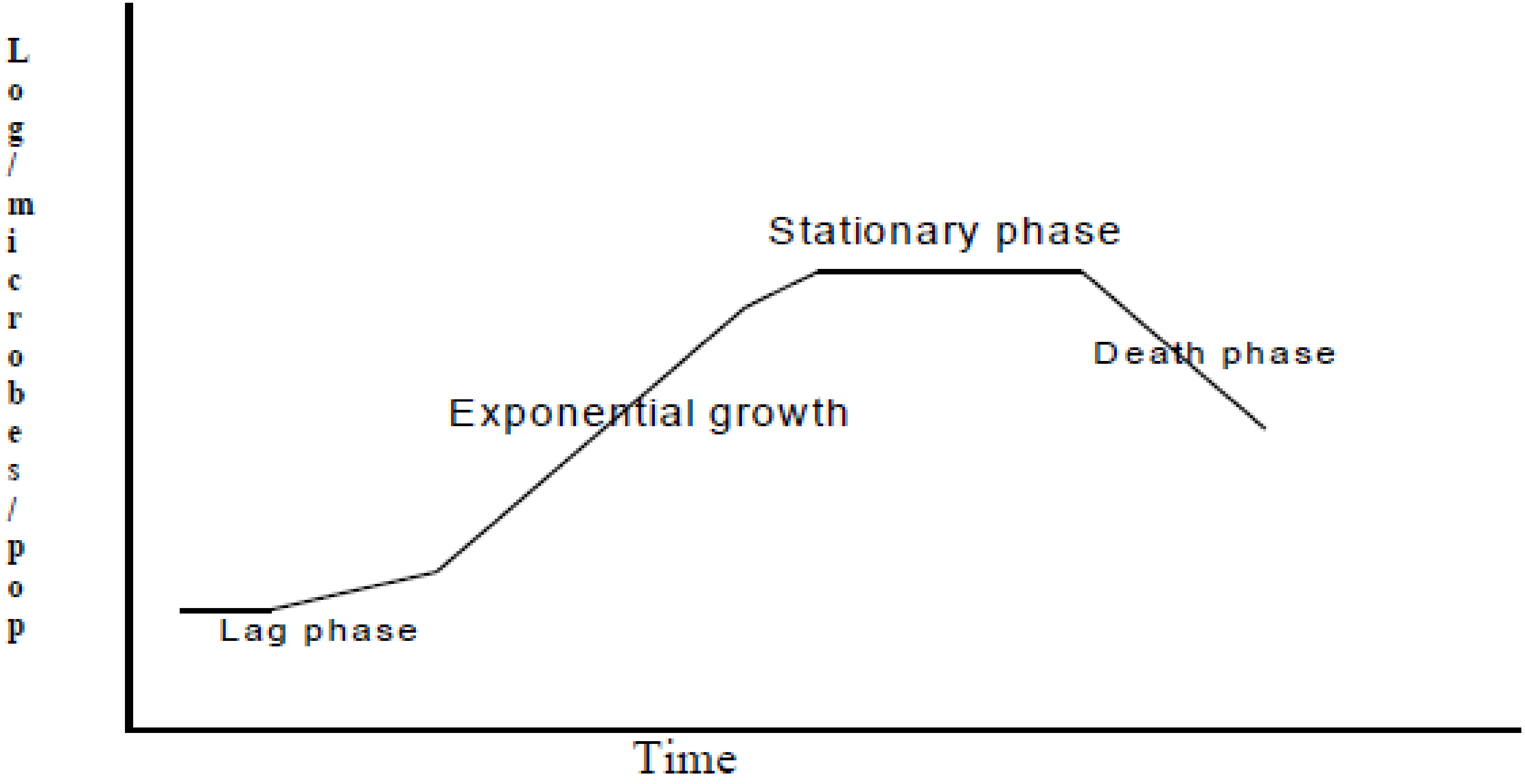


Factors that affect the patterns of growth

1. Prior exposure to organic compound substrate reduces the adaptation or the lag time

- Thus **lag times** in pristine environments should generally be much longer than in locations which have been previously exposed.

2. Initial numbers of suitable species

- Areas with larger microbial communities should require relatively short lag times to develop a viable population of degrading microorganisms.

3.The presence of more easily degraded carbon sources

- May delay the adaptation of the microbial community to more persistent contaminants.
- For example, it has been found that microorganisms degraded added glucose completely before degrading hydrocarbons in lake water.

4.Concentration of organic compound

- There may be concentration thresholds below which adaptation doesn’t occur.
- On the other hand, too high a concentration of the organic compound may be toxic to the organisms.

Cont,

- A **xenobiotic** is a chemical which is found in an organism but which is not normally produced or expected to be present in it.
- Examples: pollutants such as dioxins and polychlorinated biphenyls and their effect on the biota,
- because xenobiotics are understood as substances foreign to an entire biological system, i.e. artificial substances.

Abiotic Transformation and Degradation

☐Abiotic transformation

- Hydrolysis: interaction with water

- Photochemical degradation: interaction with light

-Oxidation/reduction: interaction with electron acceptors/donors

Cont.,

i) OXIDATION THROUGH COMBUSTION

- Oxygen reacts with organic compounds by oxidation processes that often involve the addition of oxygen to the molecule

$$CH_4 + 2\ O_2 \longrightarrow CO_2 + 2\ H_2O\ .$$

ii) HYDROLYSIS

- Water is present in large quantities in the environment in oceans, rivers, and streams.
- The chemical reaction of a compound with water is described as hydrolysis.

$$\mathbf{R\text{-}X + H_2O \longrightarrow R\text{-}\ OH + HX\ or\ (H^+ + X^-)}$$

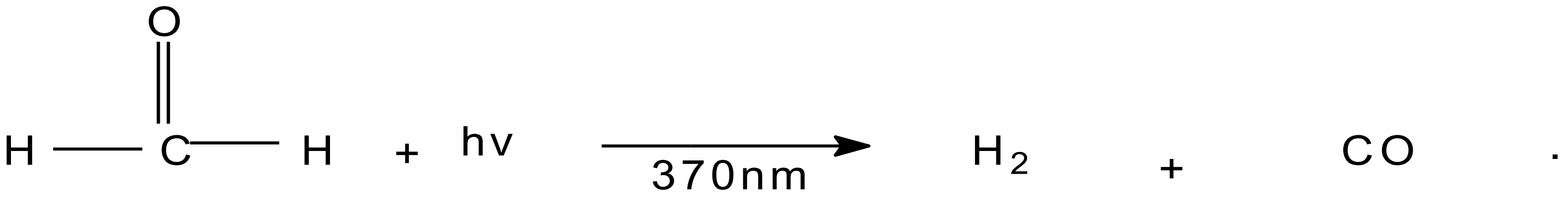
- In general, oxidation & hydrolysis may result in the production of smaller fragments that contain additional oxygen alone or both oxygen & hydrogen

iii) Photochemical transformation

- Many organic chemicals are introduced into the environment and can absorb radiation and, as a result, undergo chemical transformation

- All chemical processes require the reacting substances to have attained certain energy

☐ **Example: Transformation** of formaldehyde in to hydrogen and carbon monoxide by absorbing a solar radiation(hv) at a wavelength of 370nm



$$H-\overset{\overset{O}{\|}}{C}-H + h\nu \xrightarrow[370nm]{} H_2 + CO.$$

Oxidation and Hydrolysis

Oxidation

- Involve the addition of oxygen to the molecule.
- Example is the oxidation of methane by combustion.

$$\mathbf{CH4 + 2O2 \rightarrow CO2 + 2H2O}$$

Hydrolysis

- The chemical reaction of a compound with water

The general reaction below defines the hydrolysis process.

$$\text{R-X} \quad + \quad H_2O \quad \longrightarrow \quad \text{R- OH} \quad + \quad \text{HX} \quad \text{or } (H^+ + X^-)$$

Where R-X represent organic compound

Matters and Cycles of Matter

- **Matter** is anything that occupies space and has rest mass (or invariant mass). It is a general term for the substance of which all physical objects consist. Typically, matter includes atoms and other articles which have mass.

Cont,

- Environmental Chemistry is the study of chemical processes occurring in the environment which are impacted by humankind's activities.
- These impacts may be felt on a local scale, and global scale.
- Cycles are sequences of events that repeat themselves in a particular pattern. In environmental chemistry, our concern is basically with biogeochemical cycles.
- Some of the very important natural biogeochemical cycles include: Carbon Cycle, Nitrogen Cycle, Sulphure Cycle, and Hydrological (Water) Cycle.

Cycles of matter

- ***Cycles are sequences of reoccurring events*.**
- Cycle‘s material and energy flow (back and forth) among and within the earth‘s sub-systems.
- Organisms participate in biogeochemical cycles, which describe the circulation of matter, particularly plant and animal nutrients, through ecosystems.
- ***The flow are delicately and naturally balanced (no excess-no deficiency)***

Fundamental concepts about cycles

1. All natural cycles are governed by the **law of conservation of mass.**

2. Earthly materials are repeatedly recycled.

- The cycles can take place in global scale or local scale.

3. Cycles could be completed in fractions of seconds or millions of years.

Types of Cycles

- divided as Endogenic and Exogenic.
- ***Endogenic cycles are types of cycles,*** which predominantly involve subsurface rocks of various kinds, and
- **Exogenic cycles,** which occur largely on Earth‘s surface and usually have an atmospheric component.
- In general, sediment and soil can be viewed as being shared between the two cycles and constitute the predominant interface between them.

Hydrological or Water Cycle

- Without water there would be no life on Earth.
- All living things are made mostly of water.
- Water carries other nutrients to cells and carries wastes away from them.
- It also helps living things regulate their temperatures.
- Like all matter, water is limited on Earth.
- The water cycle let‘s living things use water over and over.

Biogeochemical cycles

These cycles interchange matter among the atmosphere, biosphere, anthroposphere, geosphere, and hydrosphere.

- ☐**Nitrogen Cycle**
- ☐**Phosphorus cycle**
- ☐**Sulphur cycle**
- ☐**Carbon cycle**

The Carbon Cycle

- The carbon cycle is the series of interconnected changes by which carbon is being continuously circulated among the natural compartments of atmosphere, biosphere, hydrosphere, geosphere and pedosphere.
- There are four major reservoirs involved in the carbon cycle. These are the plants, the terrestrial biosphere (fresh water systems and non-living organic material), the oceans (where we have dissolved inorganic carbon and living and non-living marine biota), and the sediments (including fossil fuels).
- Carbon exists as carbon dioxide (CO_2) in the atmosphere, bicarbonate ion (HCO) in water and calcium carbonate ($CaCO_3$) in carbonate rocks (limestone, chalk, coral). It is the major part of hydrocarbon molecules in petroleum and natural gas; and the main constituent of coal and dead organic matters

Ways by which CO2 is released into the Atmosphere

- Some of the ways by which CO2 is released into the atmosphere are:
- Respiration of plants and animals: This is an exothermic reaction involving the breaking down of organic molecules, e.g. glucose, into carbon dioxide and water $C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O + \text{energy.}$
- **Decay of plants and animals:** Fungi and bacteria breakdown the carbon compounds i.e. carbohydrates, proteins and lipids in dead plants and animals, and convert the carbon to carbon dioxide in the presence of oxygen or carbon dioxide and methane (CH4) in the absence of oxygen e.g.

$$C_6H_{12}O_6 \xrightarrow{\text{Methanogens}} 3CO_{2(g)} + 3CH_{4(g)}$$

cont.

- **Fermentation of carbohydrates:** The enzymatic decomposition of carbohydrates produces CO2 as a by-product

$$C_6H_{12}O_{6(aq)} \xrightarrow{\text{Zymase}} 2C_2H_5OH_{(aq)} + 2CO_{2(g)}$$

- **Burning of fossil and agro fuels:** Combustion of fossil fuels like petroleum products, coal, natural gas and agro fuels releases CO2 (and water vapour) into the atmosphere.

$$C_5H_{12} + 8O_2 \longrightarrow 6H_2O + 5CO_2$$

- **Thermal decomposition of carbonate rocks or limestone:** When limestone soils are heated up or during the production of cement, CO2 is released into the atmosphere.

$$CaCO_{3(s)} \xrightarrow{\text{heat}} CaO_{(s)} + CO_{2(g)}$$

- **Warming of surface waters:** This leads to the releasing of dissolved CO2 back into the atmosphere.
- **Volcanic eruptions:** During volcanic eruptions, the volcanic gases released into the atmosphere include water vapour, CO2 and SO2.

Ways by which CO2 is removed from the Atmosphere

Photosynthesis: Primarily, photoautotrophs (plants and algae) use light energy to convert CO2 and water to organic molecules like glucose and other carbohydrates.

To a less extent, chemoautotrophs (bacteria and archaea) convert CO2 and water to organic matter using energy derived from the oxidation of molecules of their substrates.

$$6CO_2 + 6H_2O \longrightarrow C_6H_{12}O_6 + 6O_2$$

Formation of carbonic acid: Carbon dioxide dissolves in rain water and droplets pass through the atmosphere.

Eutrophication

- The water is so **rich in nutrients** that it causes certain water plants, such as green algae, to grow extensively.

☐ As a result the **oxygen supply in the water depletes**, causing fish and other oxygen-dependent organisms to die and bacteria that are not oxygen dependent (anaerobic) to take over.

☐ When the trees are removed the rain washes phosphates away, causing the ground to become unproductive.

Decomposition and combustion

- Fungi and some bacteria get their energy by **breaking down wastes and dead organisms**. This process is called **decomposition**.
- When organisms decompose organic matter, they return carbon dioxide and water to the environment.
- When organic molecules, such as those in wood or **fossil fuels, are burned**, it is called **combustion**. Combustion releases the carbon stored in these organic molecules back into the atmosphere.

Questions

1. The application of chemistry in industry have had a major effect on human society. Which chemical applications have had the greatest impact on the human and natural environment.

2. Explain the major Environmental transformation and degradation processes

3. Indicate all the interactions between the components of environment

4. List the most important impacts of man on the environment and the vice-versa

Questions---cont'd

5. Discuss the history of environmental chemistry, its definition, and roles in the study of environmental science
6. Explain the basic properties of chemicals in the Environment
7. What general physical and chemical properties would you expect in a compound which has become a global pollution problem.

Quiz 1

1. List some environmental conditions and their mechanism, that affect transformation, biodegradations and bioavailability of a substances?
2. Define the following terms:
   a) Eutrophication
   b) Degradation
   c) Transformation

Assignment 1

1. Define the partition coefficient k_{ow} and describe how it could be used to model contaminant uptake or elimination.

- K_{ow} ($K_{octanol/water}$) describes the partition of a given contaminant (or other compound) between an n-octanol phase and a water phase at equilibrium.
- The K_{ow} (or $\log K_{ow}$) for a compound can be used to predict its lipophilicity (or hydrophobicity), which can be used, in turn, to predict its tendency to be taken up and retained by living organisms.

❑Environmental chemistry and Toxicology
(**Chem 3114**).

➢Course to be offered; to Chemistry BSc students

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Chapter 2

□Fundamentals of Aquatic Chemistry

In this Chapter we are interested in;

- Sources and uses of water,
- Properties of water,
- Chemical phenomena in water bodies,
- Gases in water (O_2, CO_2),
- Water acidity, water alkalinity,
- Redox reaction in water,
- Water quality,
- Water quality parameters (physical, chemical and biological), and
- Types of water pollutants and classes of pollutants.

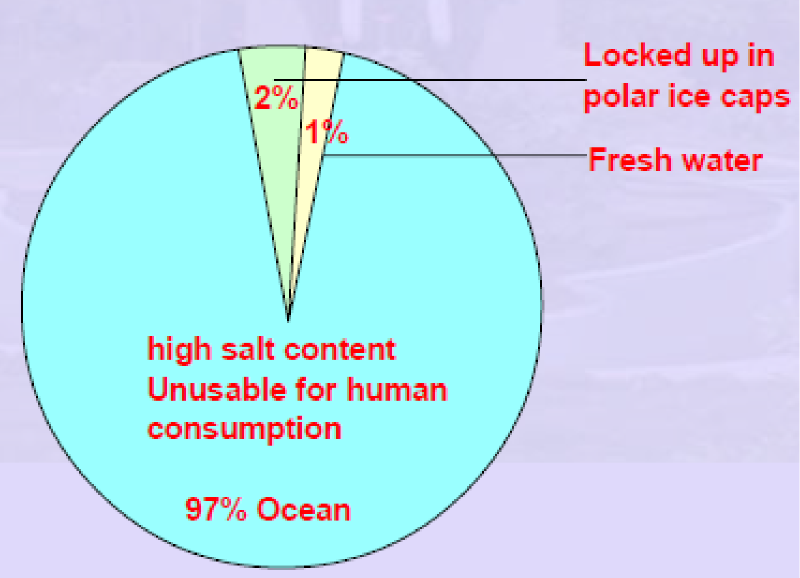
Water

- Water appears to be the most essential of the three indispensable matters (air, water and food) to man.
- Water is a vital natural resource that is essential for multiplicity of purposes
- Water is also needed for day-to-day running of vital domestic, industrial and agricultural activities.

- hence, having a good understanding of chemistry and analysis of water is vital to sustainability of man and his various activities (in the face of the fact that less than 2percent of the total water available on the surface of the earth is suitable for drinking).

Chapter 2. Aquatic Chemistry and Water pollution

❖Sources and uses of water



❖Apart from its 2 percent, technological advancement and rapid industrialization with their concurrent pollution tendencies have placed the limited good water under serious stress.

❖requires some understanding of the sources, transport, characteristics, and composition of water.

Sources and uses of water:
The Hydrologic Cycle

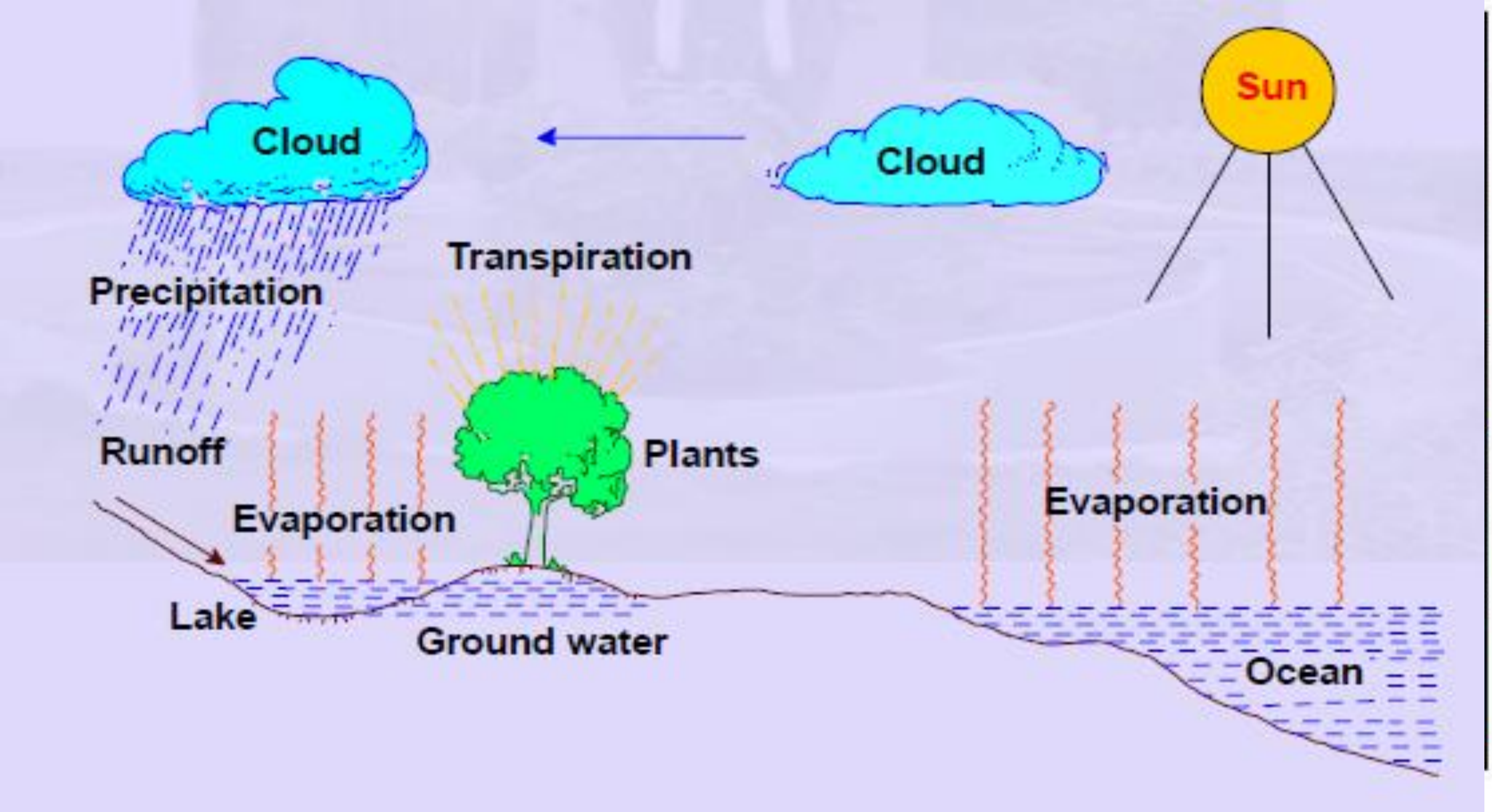


Figure 2.1.1 The hydrologic cycle

❖Factors that determine the chemistry of water body

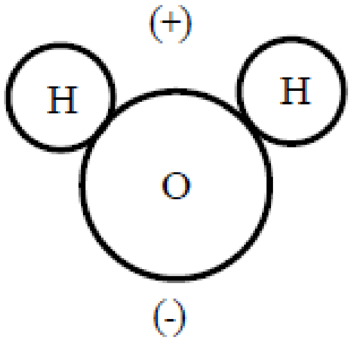
- **Place** :The chemistry of water exposed to the atmosphere is quite different from that of water at the bottom of lake
- **Micro-organisms** :Play an essential role in determining the chemical composition of water
- **Medium of the body can be:** Neutral/acidic/basic/redox/etc

❖Terms related to water chemistry

- **Hydrology** study of water
- **Limnology** studies the physical, chemical and biological characteristics of fresh water
- **Oceanography** studies about the physical and chemical characteristics of ocean

The Water Molecule

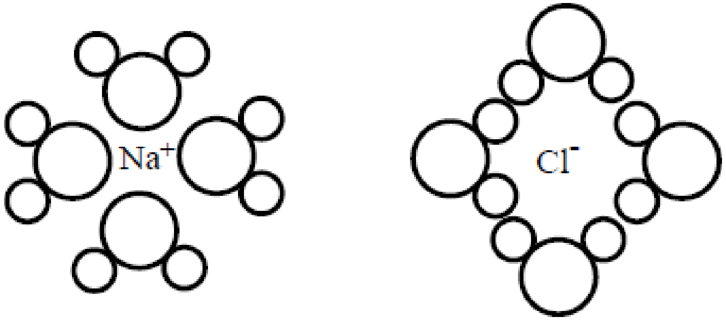
- Because of water’s bent structure and the fact that the oxygen atom attracts the negative electrons more strongly than do the hydrogen atoms,



- the water molecule behaves like a **dipole** having opposite electrical charges at either end.
- The water dipole may be attracted to either positively or negatively charged ions.

For example, When NaCl dissolves in water

- The positive sodium ions are **surrounded** by water molecules with **their negative ends pointed** at the ions, and the chloride ions are surrounded by water molecules with their positive ends pointing at the negative ions,



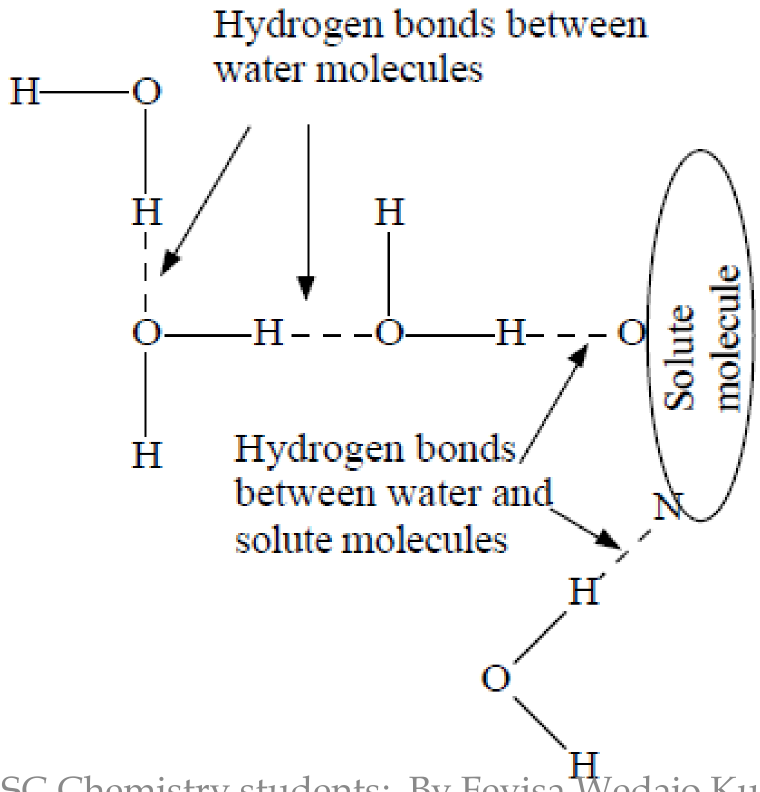
- This kind of attraction for ions is the **reason why water dissolves many ionic** compounds and salts that do not dissolve in other liquids.

THE PROPERTIES OF WATER, A UNIQUE SUBSTANCE

- Water has a number of unique properties that are essential to life.
- Some of the special characteristics of water include its
  - Polar character,
  - Tendency to form hydrogen bonds, and
  - Ability to hydrate metal ions.

hydrogen bonds.

- Hydrogen bonds are a special type of bond that can form between the hydrogen in one water molecule and the oxygen in another water molecule.



The Properties of water, a unique substance

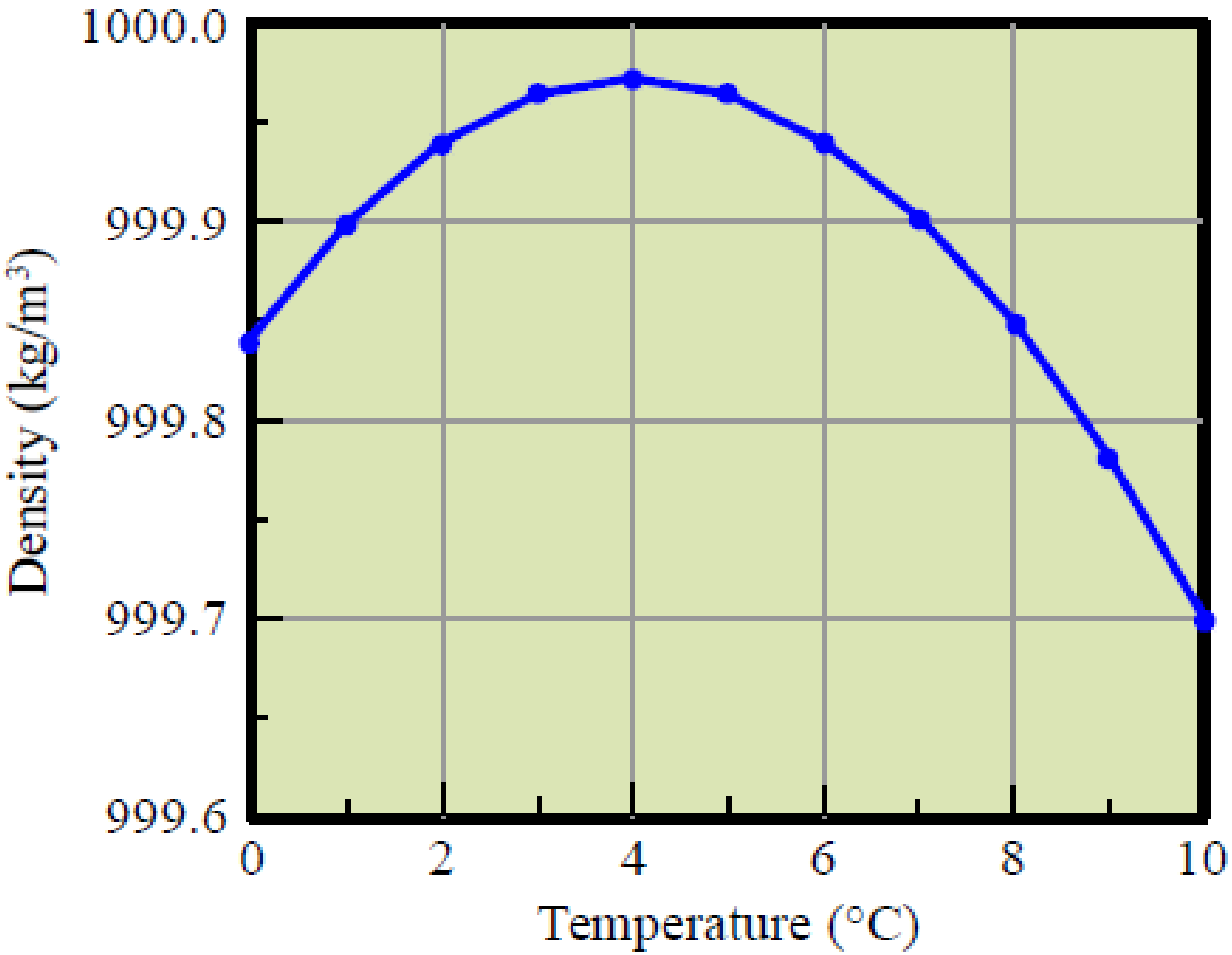
1. Density
2. Melting and Boiling points
3. Specific Heat
4. Heat of vaporization
5. Water as a solvent
6. Water has the highest dielectric constant
7. Water has the higher surface tension than common liquids
8. Water is transparent to visible & longer wavelength fraction of ultraviolet light

The Properties of water, a unique substance ---cont'd

i) Density

- Water is the only common substance that expands when it freezes.
- Maximum density as a liquid at 4^0C, which means that for temperatures above and below this point, water continuously becomes lighter and more buoyant.
- As a result, ice floats.
- If it did not, ice that would form on the surface of bodies of water would sink to the bottom
- The unusual density characteristics of water also lead to **thermal stratification of lakes,** affecting life in unusual ways.
- The expansion of water as it freezes also contributes to the weathering of rocks by literally breaking then apart when water freezes in the cracks.

Highest density at 4°C



- Ice floats on water
- Limited vertical circulation in ice covered water bodies

The Properties of water, a unique substance ---cont'd

ii) Melting and boiling points

- If water were similar to other substances (**such as H_2S, H_2, Se, & H_2Te)** it would boil at normal earth temperatures, thus existing mostly as a gas rather than a liquid or solid.

- It also has an unusually high difference in temperature between the melting point and boiling point, thus remaining a liquid over most of the globe.

- With only slightly different phase change temperatures, **life on earth** would be very different, if it could exist at all.

Unusually high boiling and freezing points

Compound	MW	Boiling Point	Freezing Point
Hydrogen Telluride (H_2Te)	129	−2°C	−49°C
Hydrogen Selenide (H_2Se)	80	−42°C	−64°C
Hydrogen Sulfide (H_2S)	34	−60°C	−84°C
Water (H_2O)	18	100°C	0°C

- Due to polar molecule and hydrogen bound
- Only inorganic liquid at room temperature

The Properties of water, a unique substance ---cont'd

iii) Specific Heat

- The specific heat of water (4184J/kg$^{0}{}_{C}$) is **higher than** it is for any other known liquid except ammonia.
- it is five times higher than the specific heat of most common heavy solids, such as rock & concrete.

☐ This effects stabilization of temperatures of organisms and geographical regions

- This property means that water heats & cools slowly than almost anything else.
- This helps moderate climate near large bodies of water, and it also serves the important function of protecting life from rapid thermal fluctuations, which are often lethal.

Highest heat capacity (except ammonia)

$$C = \frac{Q}{\Delta T}$$

with: C = heat capacity (J/K)
Q = heat (J)
T = temperature (K)

Compound	Molar heat capacity (J mol^{-1} K^{-1})	Mass heat capacity (J kg^{-1} K^{-1})
Air (20°C)	29.19	1012
Ammonia	80.08	4700
Carbon dioxide	36.94	839
Water as ice (−10°C)	38.09	2110
Water at 25 °C	75.33	4181
Water boiling (100°C)	75.33	4181
Water steam (100°C)	37.47	2080

- Much energy required to make water hotter or cooler
- Stabilisation of temperature in the environment (living organisms, geographical regions

iv) Heat of vaporization

- The heat required to vaporize water (2258 kJ/kg) is one of the highest of all liquids.

- This high heat of vaporization means that water vapor stores an unusually large amount of energy, energy that is released when the water vapor condenses.

- This property is important in distributing heat from one place on the globe to another and is a major factor affecting the earth's climate.

Highest (latent) heat of vaporisation (enthalpy of vaporisation)

Compound	Heat of vaporisation (kJ mol^{-1})	Heat of vaporisation (kJ kg^{-1})
Acetone	31.3	538.9
Ammonia	23.35	1371
Butane	21.0	320
Diethyl ether	26.17	353.1
Ethanol	38.6	841
Water	44.00	2260

- Transfer of heat between water bodies/ecosystems and atmosphere

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The Properties of water, a unique substance ---cont'd

v) Water as a solvent

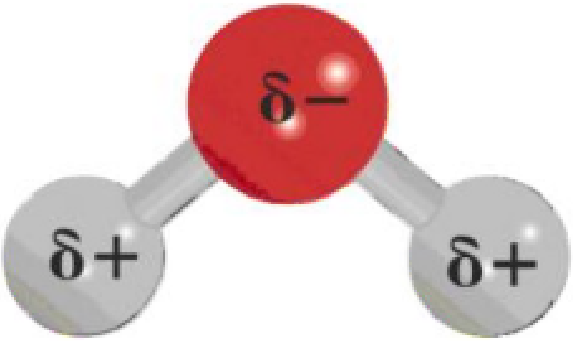
- Water dissolves more substances than any other common solvent.
- As a result, it serves as an effective medium for both transporting dissolved nutrients to tissues and organs in living things as well as eliminating their waste.
- Water also transports dissolved substances throughout the biosphere.

vi) Water has the highest dielectric constant

- This property of water equips it with **high ability to dissolve ionic substances** and their ionization in water solution.

Excellent solvent

- Polar molecule
- High dielectric constant



Compound	Dielectric constant (20°C)
Vacuum	1
Glass	5-10
Liquid ammonia (−78°C)	25
Water	80.04

- More substances dissolve in water than in any other solvent
- Water is a medium for transport of nutrients and waste products
- High solubility of ionic compounds

The Properties of water, a unique substance --- cont'd

vii) Water has the higher surface tension than common liquids

- Water is a **controlling factor in physiology** & because of its high surface tension this & other surface phenomena govern drops too.

➢ They can form a thin film over solid surfaces

Examples

Highest surface tension (apart from mercury)

Compound	Temperature (°C)	Surface tension (mN m^{-1})
Acetic acid	20	27.60
Acetone	20	23.70
Ethanol	20	22.27
Mercury	15	487.0
Water	0	75.64
Water	25	71.97
Water	50	67.91
Water	100	58.85

- Water forms droplets
- Provides strength to drops: erosion
- Controlling factor in physiology

viii) Water is transparent to visible & longer wavelength fraction of ultraviolet light

- Photosynthesis is possible at depth.

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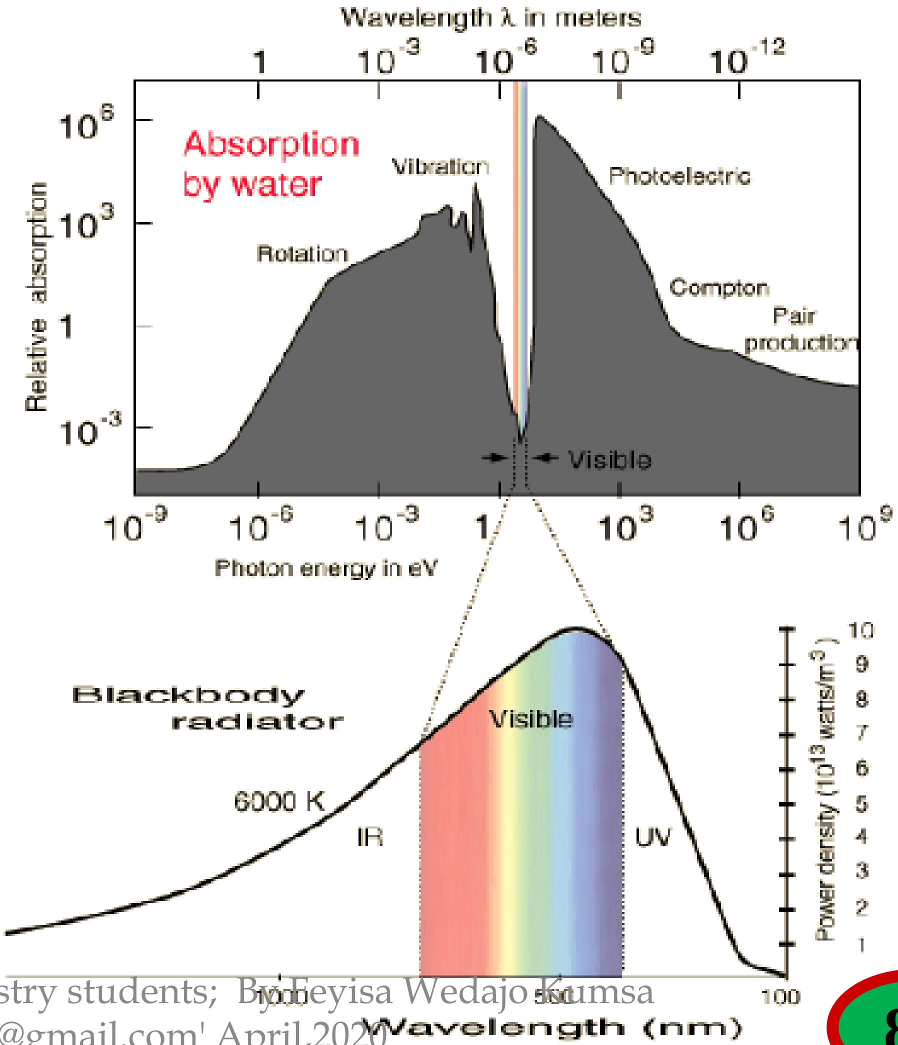
Transparent for visible light

- Water is strongly absorbing at many wavelengts (protection against radiation) but is transparent for visible light
- Light can penetrate water bodies to allow for photosynthesis



Types of water bodies

Surface & ground waters

- Surface waters(Example: Rivers, Streams, Lakes and reservoirs).

Wetlands

- flooded areas in which the water is shallow enough to enable growth of bottom-rooted plants

Estuaries

- arms of the ocean into which steams flow
- breeding grounds of much marine life

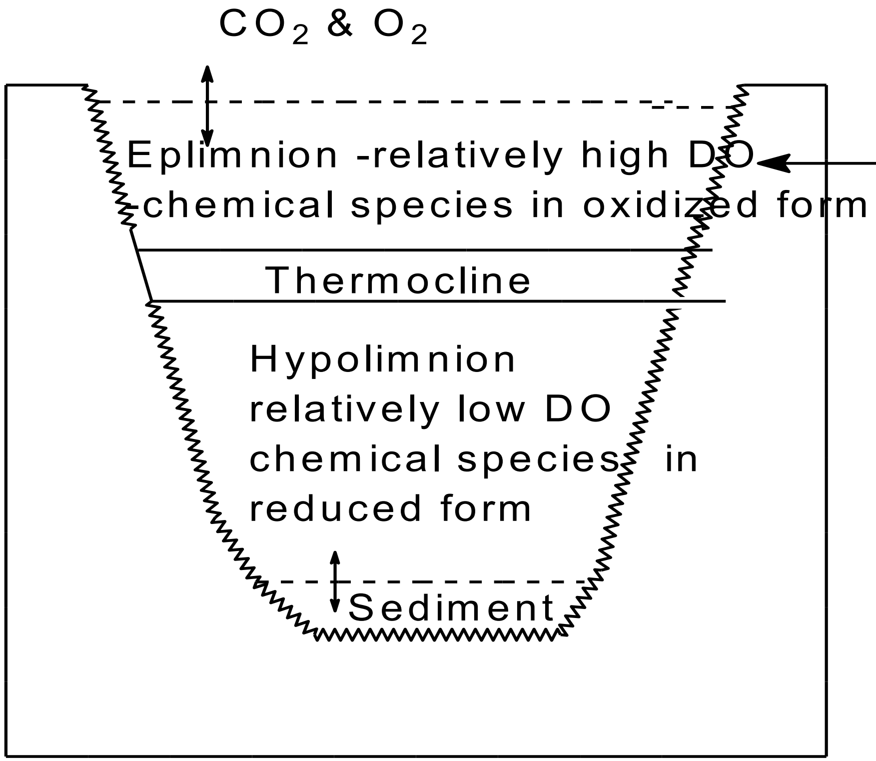
Classifications of Lakes based on productivity, nutrient content for growth(Trophic concept)

Results of the production and accumulation of organic matter

1. **Dystrophic Lakes**
    - Shallow and input of nutrients from outside of the lake
    - clogged with plant life
    - normally contain colored water with low pH
    - an input of organic acids (e.g. humic acids) from the breakdown of leaves and evergreen needles
2. **Eutrophic Lake~2.5m**
    - have more nutrients
    - known to support more life
    - more turbid and high productivity
3. **Oligotrophic Lakes~10m**
    - deep
    - generally clear
    - deficient in nutrients
    - no much biological activities
    - Low productivity

Characteristics of bodies of water

- The physical condition of a body of water strongly influences the chemical and biological processes that occur in water => thermal stratifications= Tepm profile of different density



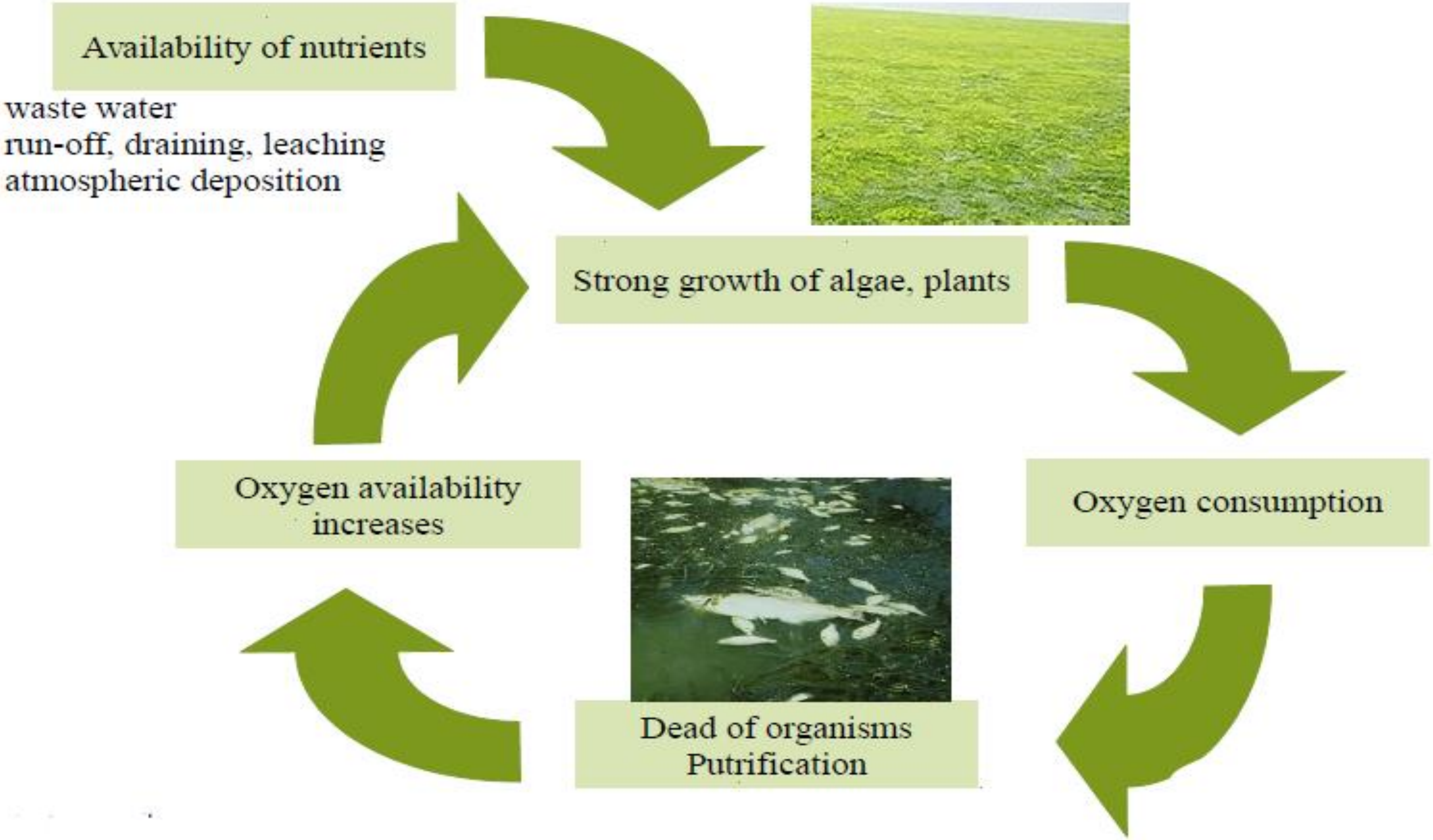
Stratification of a lake

$$CO_2 + H_2O \xrightarrow{hv} \{CH_2O\} + O_2$$

Photosynthesis

This disappearance of thermal stratification causes the entire body of water to behave as a hydrological unit, and the resultant mixing is known as **overturn**

Eutrophication



Availability of nutrients

waste water
run-off, draining, leaching
atmospheric deposition

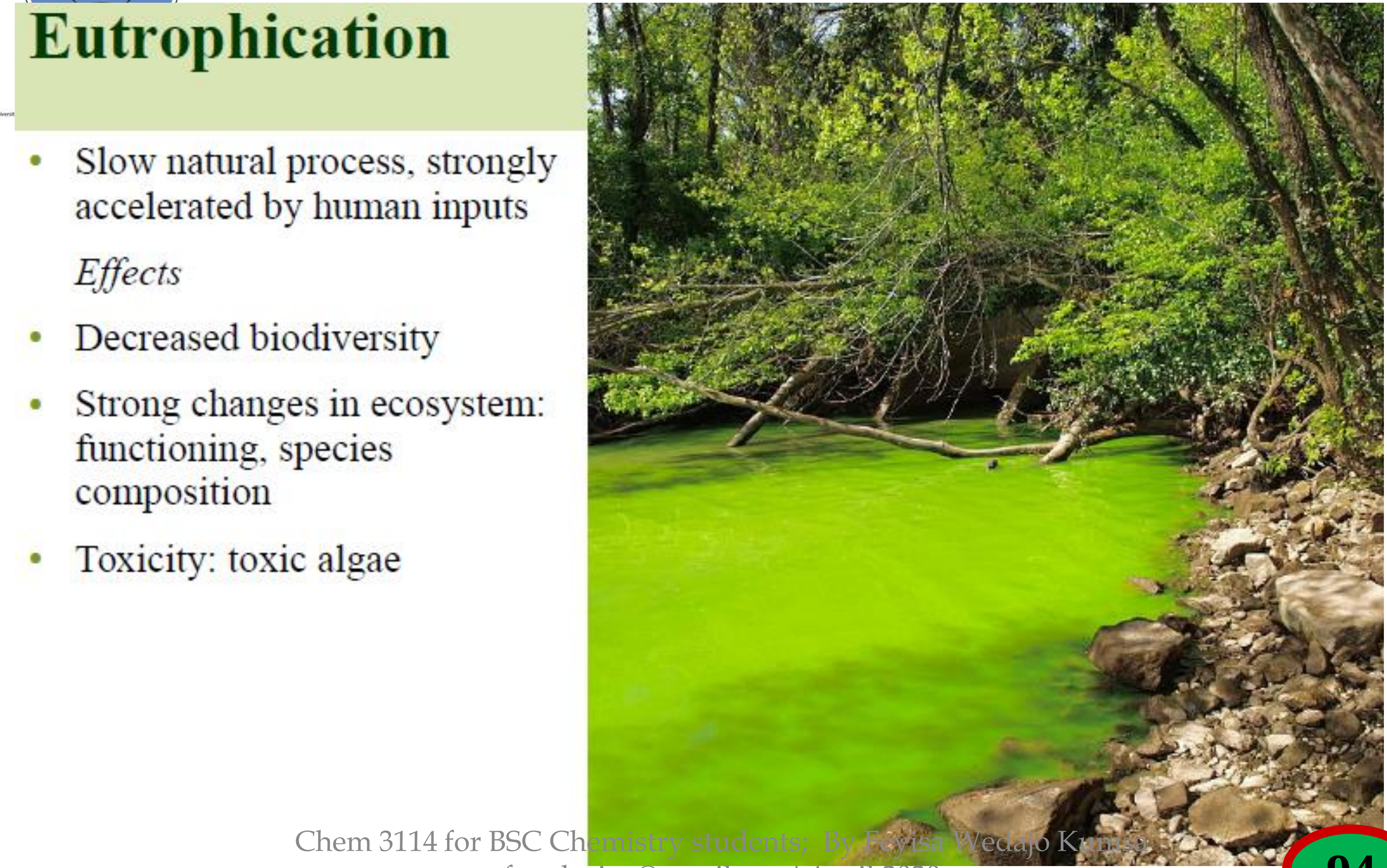
Strong growth of algae, plants

Oxygen consumption

Dead of organisms
Putrification

Oxygen availability increases

Cont.,



Eutrophication

- Slow natural process, strongly accelerated by human inputs

Effects

- Decreased biodiversity
- Strong changes in ecosystem: functioning, species composition
- Toxicity: toxic algae

Factors that affect aquatic life

1. Temperature, transparency, and turbulence
2. Dissolved Oxygen(DO)
3. Biochemical Oxygen Demand(BOD)
4. Salinity

- **Temperature, transparency, and turbulence are the three main physical properties affecting aquatic life.**
  - Very high temperature is fatal to most organisms.
  - The transparency of water is particularly important in determining the growth of algae.

Factors that affect aquatic life---cont'd

- **Turbulence** is an important factor in mixing processes and transport of nutrients and waste products in water.
  - Some small organisms (planktons) depend upon water currents for their own mobility.

- **Dissolved Oxygen, DO**, frequently is the key substance in determining the extent and kinds of life in a body of water.
  - Oxygen deficiency is fatal to many aquatic animals such as fish.
  - The presence of oxygen can be equally fatal to many kinds of anaerobic bacteria.

❖Biochemical Oxygen Demand, BOD

refers to the amount of oxygen utilized when the organic matter in a given volume of water is **degraded biologically**.

- Carbon dioxide is produced by respiratory processes in water and sediments and can also enter water from the atmosphere.
- Carbon dioxide is required for photosynthetic production of biomass by algae and in some cases is a limiting factor.

- High level of carbon dioxide produced by the degradation of organic matter in water can cause excessive algal growth and productivity.

WATER QUALITY

- Water is most abundant compound
- Several factors serve to limit the amount of water available for human use: **WATER QUALITY**

- A major objective in water quality control work is to reduce the incidence of water-related diseases.

- This objective depends on the ability to provide: water free from:
  - visible suspended matter
  - excessive color, taste and odor
  - objectionable dissolved matter
  - aggressive constituents
  - bacteria indicative of faecal pollution

Water quality

□ Condition of the water, including physical, chemical and biological characteristics

- **Requirements** are a function of particular purpose (“clean” surface and ground water, drinking, swimming, particular purpose)
- **Poor quality**

□ – Risk for human health

□ – Risk for ecosystem functioning

□ – Issues upon particular application

Quality criteria for drinking water (WHO,2004)

☐ pH	6.5 – 8.5
☐ Turbidity	5NTU
☐ F-	1.5mg/l
☐ Oxygen demand	5 mg O2/l
☐ As	0.001mg/l
☐ Calcium	75 mg/l
☐ Electrical conductivity	< 250 µS/cm
☐ Nitrite ($NO^{2–}$)	0.10 mg/l
☐ Ammonium (NH_4+)	0.50 mg/l

Magnesium	50 mg/l
Sodium	200 mg/l
Chloride	< 250 mg/l
Sulfate	< 250 mg/l
Nitrate ($NO^{3–}$)	50 mg/l

WATER CHEMISTRY AND Quality

- **Physical Parameters Relevant to Water Quality Analysis**
- Turbidity
- Color
- Taste and Odor
- Temperature
- Solids in Water Supplies

Total solids

❑ Inorganic and organic solids present in the water

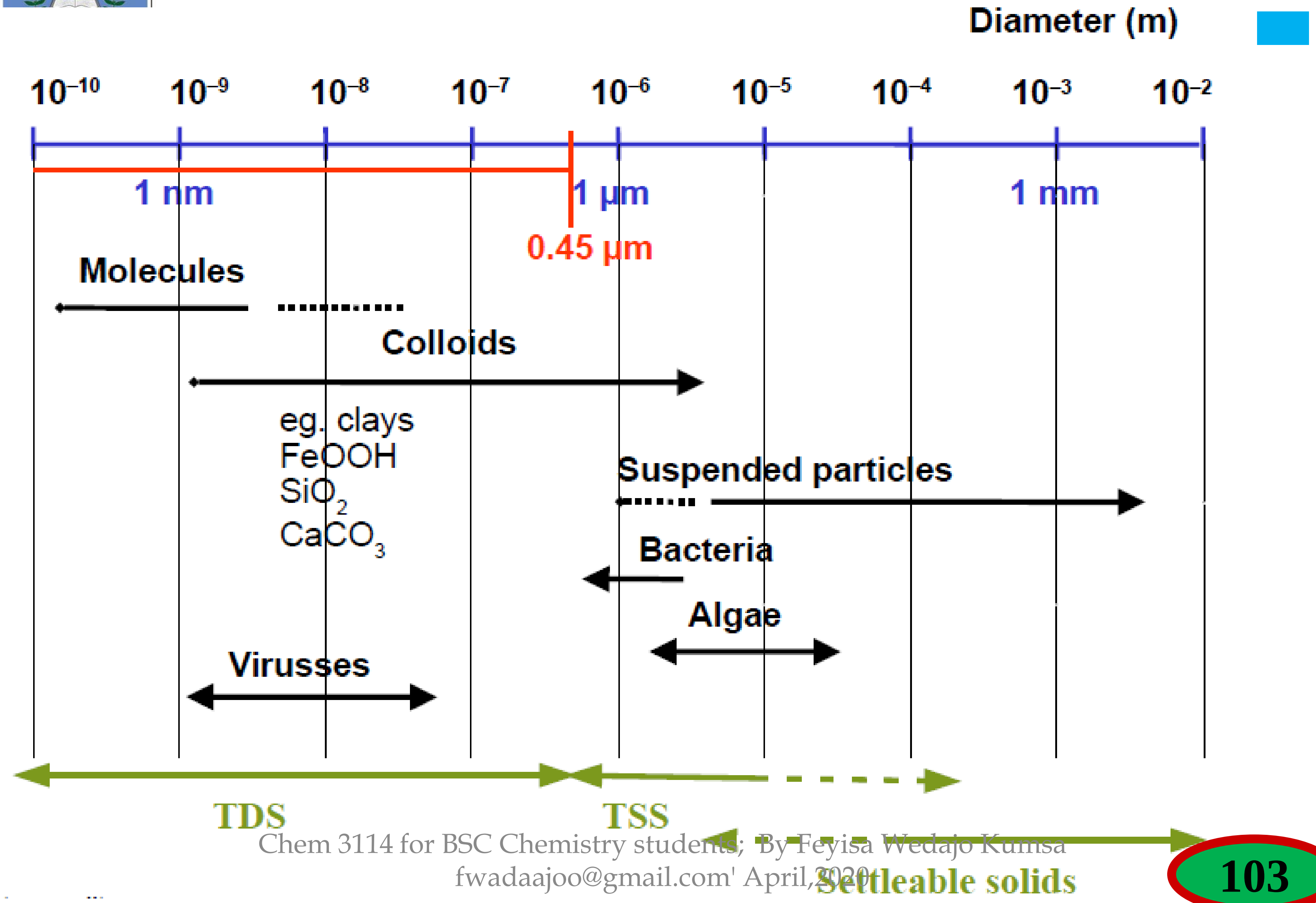
➢ – Total dissolved solids (TDS)

- "dissolved" in water
- – Total suspended solids (TSS) "suspended" infinitely in water (i.e. colloids)

➢ – Settleable solids

☐ Solids that will not remain suspended

Dissolved and suspended particles



Total dissolved solids

❑Truly in solution”

- Solution transparent (can be coloured)
- Operationally defined as particles passing a 0.45 (or 0.2 ...) µm filter

☐ Dissolved salts: cations, anions

☐ Molecules

☐ very small agglomerations

- Derived from

– Weathering and dissolution of rock and soils

– Contamination, run-off (e.g pesticides)

Measurement of total dissolved solids

- **Gravimetry**
  - – Filter through 0.45 μm membrane filter
  - – Evaporate the liquid
  - – Determine mass of solid residue
- *Most accurate method, but time consuming*
- Conductivity
  - – Measure electrical conductivity which is directly related to concentration of dissolved ionic salts
- Proxy for TDS
  - – Actual relation between conductivity and TDS depends on nature of dissolved salts (provided salts are the dominant fraction of TDS)

Relation to total dissolved solids

- Specific conductivity ~ dissolved ions ~ dissolved salts
- Rules of thumb

$$\text{TDS (mmol/l)} = 10 \times \text{EC (mS/cm)}$$

$$\text{TDS (mg/l)} = 640 \times \text{EC (mS/cm)}$$

Problem 1

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1. A water sample has an electrical conductivity of 780 µS/cm. What is the approximate concentration of total dissolved salts in the solution?

Total suspended solids (TSS)

□Particles suspended in the water (colloids in stable suspension)

- May cause turbidity
- **Gravimetric analysis**

– Weigh membrane filter (kept in desiccator)

– Filtrate water through 0.45 µm membrane filter

– Weigh filter + sediment

Turbidity

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- The term **“turbid”** is applied to waters containing suspended matter that interferes with the passage of light through the water or in which visual depth is restricted.
- Turbidity may be caused by a wide variety of suspended materials ranging in sizes from colloidal to coarse dispersions, depending upon the degree of turbulence.
- **Method of Turbidity Determination**

Nephelometry (NTU)

Turbidity

- “True” solution is transparent (though perhaps coloured).
- Suspension is turbid because passing light is scattered in all directions

Significance of Turbidity in Public Water Supplies

- **Aesthetics**: Any turbidity in a sample of drinking water is automatically associated with possible wastewater pollution and the health hazards occasioned by it.
- **Filterability**: Filtration of water is rendered more difficult and costly with increasing turbidity.
- **Disinfection**: To be effective, there must be direct contact between a given disinfectant (e.g. chlorine, ozone, chlorine dioxide or UV radiation) and the organisms it has to kill.

color

- Color caused by suspended matter is referred to as **apparent color** while
- color caused by vegetable or organic extracts that are colloidal is called **true color**
- **Significance of color in public water supplies**
  - **Disinfection** problem.
  - Problem of **aesthetic unacceptability**.

Chemical Parameters in Water Chemistry

- ❑Some Relevant Chemical Parameters of Water
- □pH
- □Acidity
- □Alkalinity
- □Hardness

Cont.,

- pH is a term used to express the intensity of the acid or alkaline condition of a solution.
- Acidity is a measure of the ability of a given water sample to neutralize strong bases to an indicator end point.

Sources and Nature of Acidity

- Carbonic and its species are formed when CO_2 enters surface waters.
- This happens when concentration of CO_2 in water is less than that in equilibrium with CO_2 in the atmosphere.
- Bacterial oxidation of organic matter
- Mineral acidity

$$2S + 3O_2 + 2H_2O \longrightarrow \text{bact.}\ \ 4H^{+} + 2SO_4^{2-}$$

$$FeS_2 + 3\tfrac{1}{2}\,O_2 + H_2O \longrightarrow \text{bact}\ \ Fe^{2+} + 2H^{+} + 2SO_4^{2-}$$

Alkalinity

- The alkalinity of a water sample is a measure of its capacity, to neutralize acids.
- Constituents of alkalinity in natural water systems

include CO_3^{2-}, HCO_3^-, OH^-, $HSiO_3^-$, $H_2BO_3^-$, HPO_4^-, HS^- and NH_3^0.

- These compounds result from the dissolution of mineral substances in the soil and atmosphere.
- Phosphates may also originate from detergents in waste water discharges and from fertilizers and insecticides from agricultural land.
- Hydrogen sulphide and ammonia may be products of microbial decomposition of organic material.

Alkalinity Cont.,

- The most common constituents of alkalinity are:
  - bicarbonate(HCO_3^-),
  - carbonate (CO_3^{2-}) and
  - hydroxide (OH^-).
- In addition to their mineral origin, these substances can originate from CO_2, a
  - constituent of the atmosphere and
  - a product of microbial decomposition of organic material

Cont., Alkalinity due to CO2 according to the following reactions.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \text{ (dissolved } CO_2 \text{ and carbonic acid)}$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \text{ (bicarbonate)}$$

$$HCO^-_3 \rightleftharpoons H^+ + HCO_3^{2-} \text{ (carbonate)}$$

$$CO^{2-}_3,\ H_2O \rightleftharpoons HCO_3^- + OH^- \text{ (hydroxide).}$$

Hardness of water

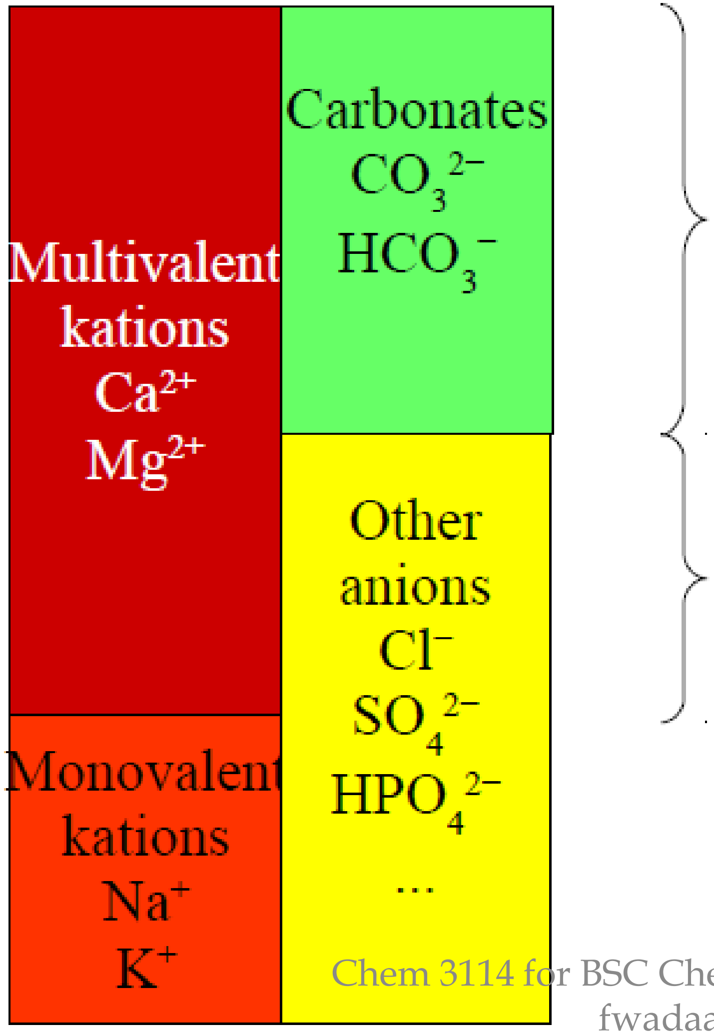
- ❑ *Traditional meaning*: amount of soap one needs to add to form lather
- ➢ *Cause of hardness*: presence of bivalent (or multi-) cations, mainly Ca^{2+} and Mg^{2+}
- ● *Effects*
  - ✓ Precipitation of lime stone
- □ $\mathrm{Ca}^{2+} + 2\ \mathrm{HCO3}- \rightarrow \mathrm{CaCO3(s)} + \mathrm{H2O} + \mathrm{CO2}(\uparrow)$
- ✓ Aggregation of soap micelles (fatty acids) which precipitate as scum.
- □ More soap needed for same washing effect.

Hardness

Hardness is defined as the concentration of multivalent **metallic cations** in water which determine the capacity of the water to precipitate soap.

- ☐ Depending on the anion with which it associates, hardness is classified as **calcium and magnesium hardness**, **carbonate hardness** and **non carbonate hardness** and **pseudo-hardness**.
- ☐ Other ions that may cause hardness include Fe^{2+}, Mn^{2+}, Sr^{2+} and Al^{3+}.

Permanent and temporary hardness



Multivalent kations

Ca^{2+}

Mg^{2+}

Monovalent kations

Na^{+}

K^{+}

Carbonates

CO_3^{2-}

HCO_3^{-}

Other anions

Cl^{-}

SO_4^{2-}

HPO_4^{2-}

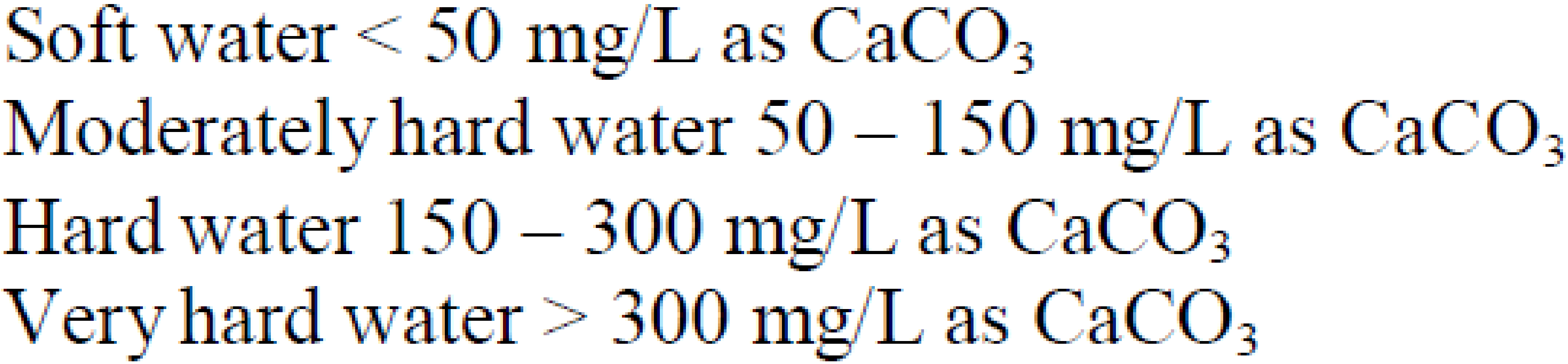
…

Temporary hardness
Disappears after boiling

$$HCO_3^{-} \rightarrow CO_2(\uparrow) + CO_3^{2-}$$
$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3(\downarrow)$$

Permanent hardness
Not removed after boiling

consumer's acclimation to hardness, a generally accepted classification is as follows(Sawyer ,1960)



Soft water < 50 mg/L as $CaCO_3$

Moderately hard water 50 – 150 mg/L as $CaCO_3$

Hard water 150 – 300 mg/L as $CaCO_3$

Very hard water > 300 mg/L as $CaCO_3$

$$[\mathrm{CaCO3}]=2.5\times[Ca2+]+4.1\times[Mg2+]$$

One degree of general hardness or German degree is defined as 10mg/L CaO

One French degree is defined as 10mg/L $CaCO_3$

Softening of water

- Ion-exchange resins
  - $R-(Na+)2 + Ca2+ \rightarrow R-Ca2+ + 2 Na+$
- Lime softening: addition of lime water ($Ca(OH)2$)
  - – Rise pH, $CaCO3(\downarrow)$, $Mg(OH)2(\downarrow)$
  - – Substantial reduction in TDS
- Chelating agents: "mask" the cations in solution (citric acid, EDTA: added in many commercial products)
- Distillation and rain water
  - – Distillation usually too expensive
- Reverse osmosis
  - – No ions being added

Problem 2

1. A surface water contains 205 mg/l Ca and 28 mg/l Mg. What is the hardness in mmol/l, ppm, in german degre of hardness, in frech degree of hardness?

In German Degrees (°D)	= 5.6*mmol/l
In French Degreed (°F)	= 10*mmol/l

Answer = 6.277mmol/l, 627.7ppm, 35.3D^{o}, 62.8F^{o}

Water quality parameters---cont'd

Biological water quality parameters

Pathogens

- **Bacteria**
- **Virus**
- **Protozoa**
- **Helminths**

Biochemical Parameters in Water Chemistry and Quality

- Dissolved Oxygen (DO)
- Biochemical Oxygen Demand (BOD)
- Chemical Oxygen Demand

DO

- Amount of oxygen dissolved in water.
- The solubility of oxygen in **saline** water is less than in **fresh water**.
- The solubility of atmospheric oxygen, in fresh waters ranges from 14.6 mg/L at 0^0C to about 7 mg/L at 35^0C under one atm of pressure.
- A stream must have a minimum of about **two mg/L** of dissolved oxygen to maintain higher life forms such as fish and other aquatic animal species.

❑**Methods of DO Determination**

- The Winkler of iodometric method (titrimetric method)
- The nitrite ion is one of the most frequent interferences encountered in DO determination of water. [by NaN_3]

Biochemical Oxygen Demand (BOD)

- The amount of oxygen consumed during microbial utilization of organics in a water sample is called the BOD.
- The greater the decomposable matter present, the greater the oxygen demand and the greater the BOD value.

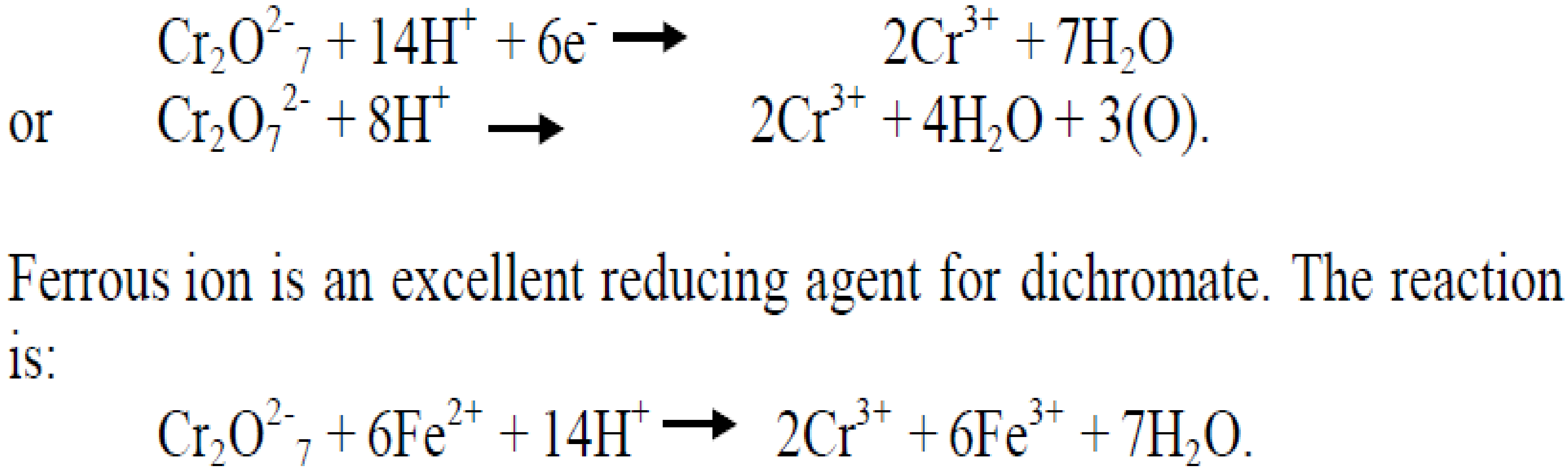
❑The BOD is measured by determining the oxygen consumed from a water sample placed in an air-tight container and kept in a controlled environment for a preselected period of time. **BOD5**

Chemical Oxygen Demand

- COD is a measure of the total amount of oxygen required for complete oxidation to CO_2 and H_2O of organic matter present in a sample of wastewater or effluent.
- COD is a rapidly measured parameter used to determine the pollution strength of domestic and industrial waste.
- The determination is achieved by using strong oxidizing agents under acidic conditions.

COD Cont.,

- Potassium dichromate, K2Cr2O7, is the most suitable oxidizing agent. The reaction is:



$$Cr_2O^{2-}{}_7 + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

or $$Cr_2O_7{}^{2-} + 8H^+ \rightarrow 2Cr^{3+} + 4H_2O + 3(O).$$

Ferrous ion is an excellent reducing agent for dichromate. The reaction is:

$$Cr_2O^{2-}{}_7 + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O.$$

Inorganic Interferences , COD test

- Cl^{-}, NO^{2-}, etc
- However, this interference can be eliminated by the addition of mercuric sulphate or sulfamic acid and NaN3 to the sample prior to the addition of other reagents.

Home Work

1) Dissolved oxygen is determined in a surface water. To 297.6 ml of water in the Winkler bottle, 1 ml MnSO4 solution and 2 ml KOH+KI are added. After acidification with H_2SO4 the solution is transferred to an erlenmeyer and titrated with 10.3 ml 0.02 *M* $Na_2S_2O_3$. What is the dissolved oxygen level in the water (mg/l)?

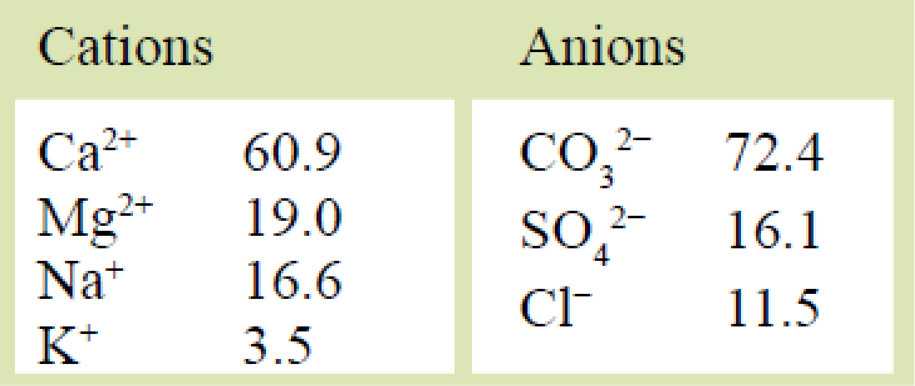
Anions and other Constituents Concern in Water Chemistry and Analysis

☐Common Anions in Natural and Wastewaters

- Chloride (Cl^-)
- Fluoride (F^-)
- Sulfate (SO_4^{2-})
- Phosphate (PO_4^{3-})
- Residual Chlorine
- Nitrogen
- Iron and Manganese in Water
- Oil and Grease in Water and Volatile Acids in Water

Chemical constituents of water

Average composition of sweet surface water (%) (Cole, 1983)

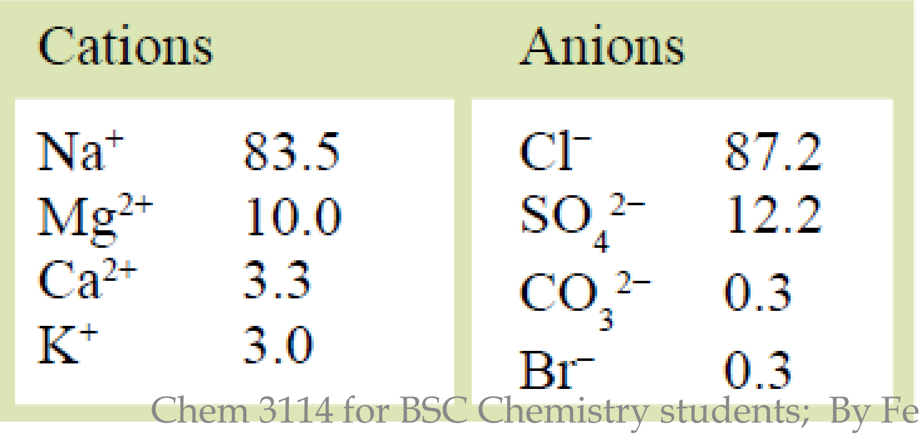


Cations		Anions	
Ca^{2+}	60.9	CO_3^{2-}	72.4
Mg^{2+}	19.0	SO_4^{2-}	16.1
Na^+	16.6	Cl^-	11.5
K^+	3.5		

TDS < 1 g/l

Average composition of sea water (%) (Cole, 1983)

TDS ~ 35 g/l



Cations		Anions	
Na^+	83.5	Cl^-	87.2
Mg^{2+}	10.0	SO_4^{2-}	12.2
Ca^{2+}	3.3	CO_3^{2-}	0.3
K^+	3.0	Br^-	0.3

Major anions

- Chloride: Cl^-

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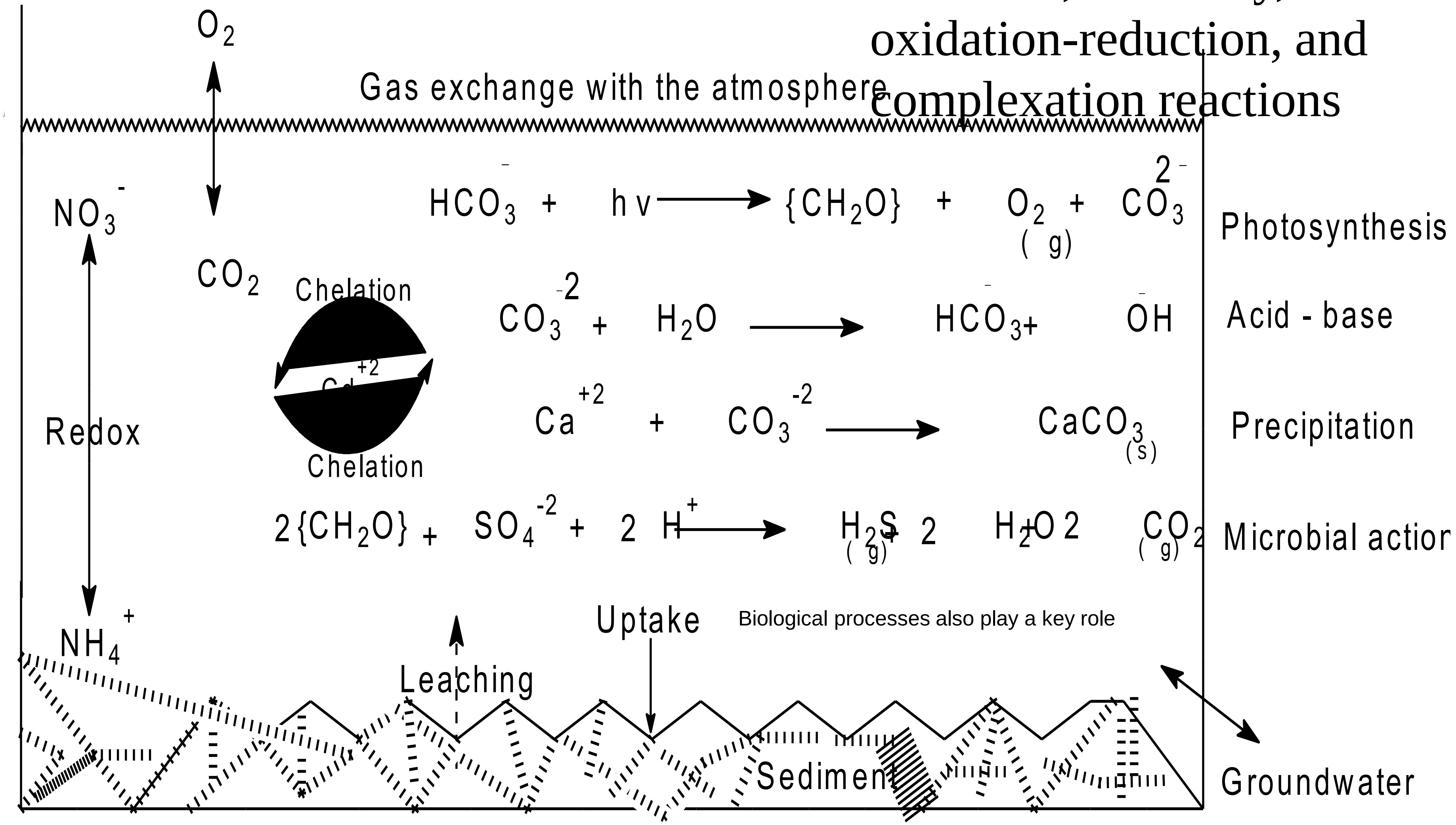
  - Sweet water: < 1 mg/l
  - Low concentrations add “palatability”. “Salty taste” from 250 mg/l onwards
  - Sea water: 20 000 mg/l
- Sulphate: SO_4^{2-}
  - In sweet water generally in higher concentrations than chloride
  - Few to several 100 mg/l
  - Taste > 600 mg/l as $CaSO_4$

Analytical determination

- Cl^{-}
  - Volumetry: titration with Ag
  - Ion chromatography
- SO_4^{2-}
  - Gravimetry ($BaSO_4$)
  - Turbidimetry ($BaSO_4$)
  - Ion chromatography

CHEMICAL PHENOMENA IN WATER BODIES

acid-base, solubility, oxidation-reduction, and complexation reactions



O_2

Gas exchange with the atmosphere

NO_3^-

CO_2

Chelation

Cd^{+2}

Chelation

Redox

$HCO_3^- + h\nu \longrightarrow \{CH_2O\} + O_{2(g)} + CO_3^{2-}$ Photosynthesis

$CO_3^{-2} + H_2O \longrightarrow HCO_3^- + OH^-$ Acid - base

$Ca^{+2} + CO_3^{-2} \longrightarrow CaCO_{3(s)}$ Precipitation

$2\{CH_2O\} + SO_4^{-2} + 2H^+ \longrightarrow H_2S_{(g)} + 2H_2O\ 2CO_{2(g)}$ Microbial actior

NH_4^+

Leaching

Uptake

Biological processes also play a key role

Sediment

Groundwater

Figure: Major aquatic chemical processes

CHEMICAL PHENOMENA IN WATER BODIES---cont'd

- Generally speaking it is not possible to exactly describe the chemistry of natural water bodies.

Solution : ***modeling*** (carefully controlled conditions of the laboratory) .

Home work / Assignment 1

1) How does azide eliminate the nitrite interference in the iodometric method for determining dissolved oxygen? Show in rxns

2) List at list three inorganic species that interfere with COD analysis, and also Which of the species is the most prevalent and how do you handle the interference caused by this particular species? Show with rxns

OXYGEN IN WATER

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- Well-being of fish & normal aquatic life
- Useful for biodegradation
- Aerobic decomposition of organic matter in polluted waters

- Water reoxygenate through
  - Contact with atmosphere
  - Photosynthesis from algae
- Solubility of O_2 depends on:
  - Water temperature
  - Partial pressure
  - Salt content of water

Carbon dioxide in water

- the most important weak acid in water
- it is found in virtually all natural waters
- influences the chemistry of water

- **Sources**
  - Atmosphere
  - Decay of organic matter

- Rain water from unpolluted atmosphere is even slightly acidic

Carbon dioxide in water---cont'd

- Influences the chemistry of water
    - It is only 0.037% by volume of normal dry air.
    - Deposition of minerals as CO_3^{2-}
    - It is used as source of carbon for algae
- The concentration of gaseous CO_2 in the atmosphere varies with location & season; it is increasing by one ppm by volume per year.
- Two equilibrium reactions that affect pH

$$CO_2(\text{water}) \rightleftharpoons CO_2(\text{atmosphere})$$

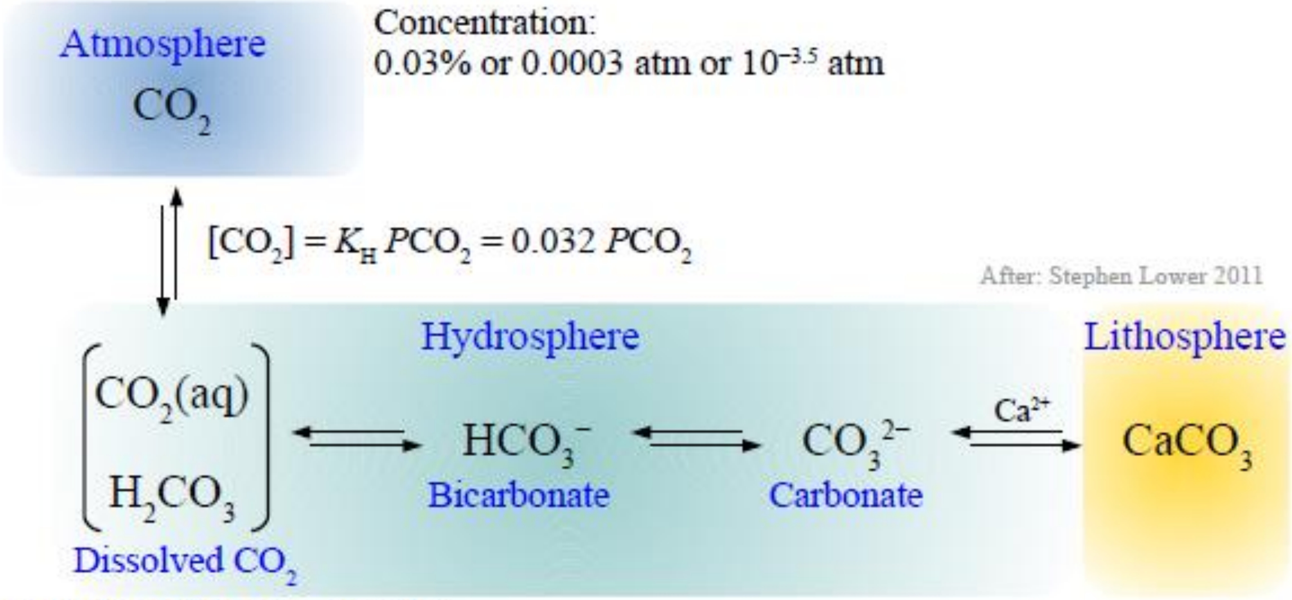
Carbon dioxide in water---cont'd

- Water with low level CO_2 lacks alkalinity
- However, the formation of HCO_3^- & CO_3^{-2} greatly increases the solubility of CO_2
- High conc. of free CO_2 in water may adversely affect
  - Respiration,
  - gas exchange &
  - May be fatal(cause death) above 25mg/L
- Large share of CO_2 in water is from decay of organic matter

❖ CO_2 is involved in limestone cave formation

$$CaCO_3\,(S) + CO_2 + H_2O \rightleftharpoons Ca^{+} + HCO_3^{-}$$

Carbonate equilibria



Atmosphere

CO_2

Concentration:
0.03% or 0.0003 atm or $10^{-3.5}$ atm

$[CO_2] = K_H\, PCO_2 = 0.032\, PCO_2$

After: Stephen Lower 2011

Hydrosphere

Lithosphere

$CO_2(aq)$

H_2CO_3

Dissolved CO_2

HCO_3^-

Bicarbonate

CO_3^{2-}

Carbonate

Ca^{2+}

$CaCO_3$

Solubility of CO_2 in pure water:
0°C: 0.077; 4°C: 0.066; 10°C: 0.054; 20°C: 0.039 mol/l

$$CO_2(g) + H_2O \leftrightarrow H_2CO_3^* \qquad \log K = -1.46$$

$$H_2CO_3^* \leftrightarrow HCO_3^- + H^+ \qquad \log K = -6.36$$

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \qquad \log K = -10.33$$

The predominant species formed by CO_2 dissolved in water depends upon pH

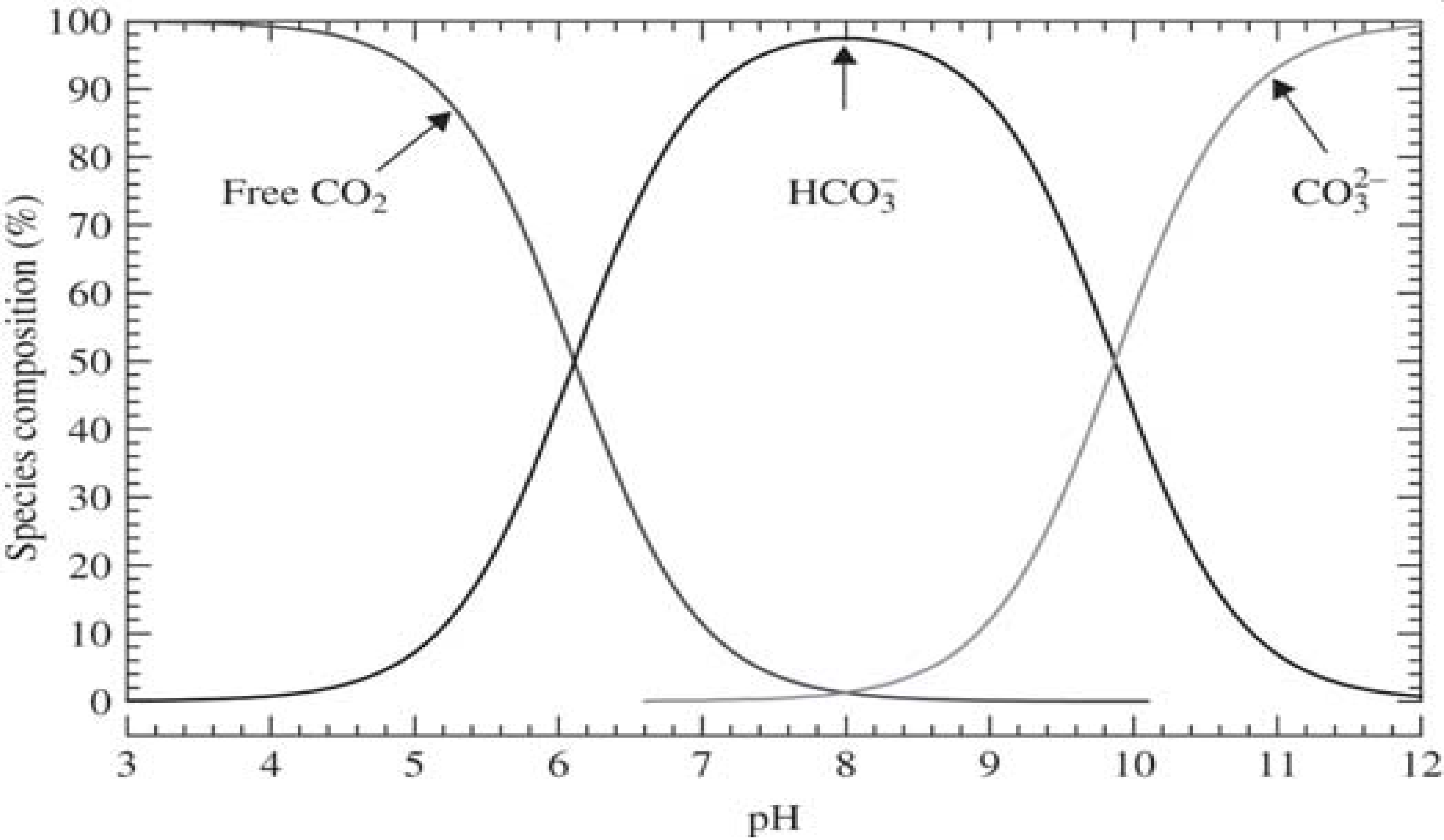


Figure: Distribution of species diagram for the CO_2–HCO_3^-–CO_3^{2-} system in water

The CO_2-HCO_3^--CO_3^{2-}system

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$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+ \;,\; Ka_1 = \frac{[H^+]\,[HCO_3^-]}{[CO_2]} = 4.45 \times 10^{-7}.$$

$$HCO_3 \rightleftharpoons CO_3^{2-} + H^+ \;,\; Ka_2 = \frac{[H^+]\,[CO_3^{2-}]}{[HCO_3^-]} = 4.69 \times 10^{-11}.$$

The CO_2-HCO_3^--CO_3^{2-}system---cont'd

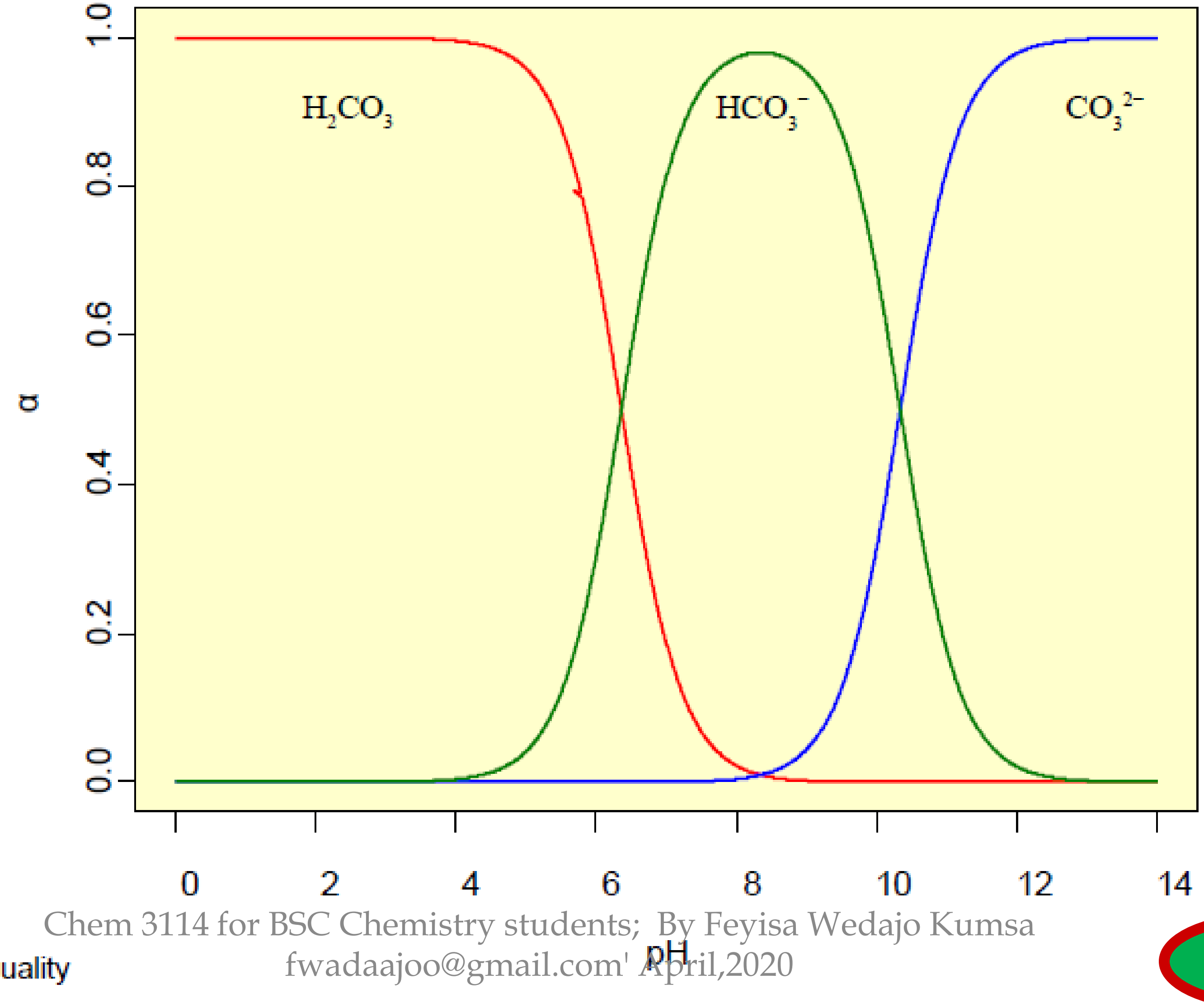
αCO_2(fraction of CO_2)=

$$\text{fraction of } CO_2 = \frac{[CO_2]}{[CO_2] + [HCO_3^-] + [CO_3^{2-}]}$$

$$= \frac{[H^+]^2}{[H^+]^2 + Ka_1 [H^+]^2 + Ka_1Ka_2}$$

Exercise: **Do the same for the fraction of bicarbonate and carbonate**

Carbonate species in solution



Carbonate forms in water

$CO_2(g) + H_2O \leftrightarrow H_2CO_3^*(aq)$ $\qquad \log K = -1.46$

$$K = \frac{(H_2CO_3^*)}{(CO_2)} = 10^{-1.46} = 3.47 \cdot 10^{-2}$$

$$\log K = -1.46 = \log(H_2CO_3^*) - \log(CO_2)$$

$$\log(H_2CO_3^*) = -1.46 + \log(CO_2(g))$$

with: $\log(CO_2(g)) = 10^{-3.5}$ atm

$\log(H_2CO_3^*) = -4.96$

Carbonate forms in water

$$CO_2(g) + H_2O \leftrightarrow H_2CO_3{}^*(aq) \qquad \log K = -1.46$$

$$H_2CO_3{}^* \leftrightarrow HCO_3{}^- + H^+ \qquad \log K = -6.36$$

$$CO_2(g) + H_2O \leftrightarrow HCO_3{}^- + H^+ \qquad \log K = -1.46 - 6.36 = = -7.82$$

$$-7.82 = \log (HCO_3{}^-) + \log(H^+) - \log (CO_2(g)) \leftrightarrow$$

$$\log (HCO_3{}^-) = -7.82 - \log (H^+) + \log (CO_2(g))$$

$$\log (HCO_3{}^-) = -7.82 + \log (CO_2(g)) + pH$$

Carbonate forms in water

$$CO_2(g) + H_2O \leftrightarrow H_2CO_3^*(aq) \qquad \log K = -1.46$$

$$H_2CO_3^* \leftrightarrow HCO_3^- + H^+ \qquad \log K = -6.36$$

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \qquad \log K = -10.33$$

$$CO_2(g) + H_2O \leftrightarrow CO_3^{2-} + 2\,H^+ \qquad \log K = -1.46 - 6.36 - 10.33 = -18.15$$

$$-18.15 = \log(CO_3^{2-}) + 2\log(H^+) - \log(CO_2(g)) \leftrightarrow$$

$$\log(CO_3^{2-}) = -18.15 - 2\log(H^+) + \log(CO_2(g))$$

$$\log(CO_3^{2-}) = -18.15 + \log(CO_2(g)) + 2\,pH$$

Quiz

1. How much CO2 can be dissolved in a surface water at PH of 6.5?

Given:

$$\log(H_2CO_3^*) = -1.46 + \log(CO_2(g))$$

$$\log(HCO_3^-) = -7.82 + \log(CO_2(g)) + pH$$

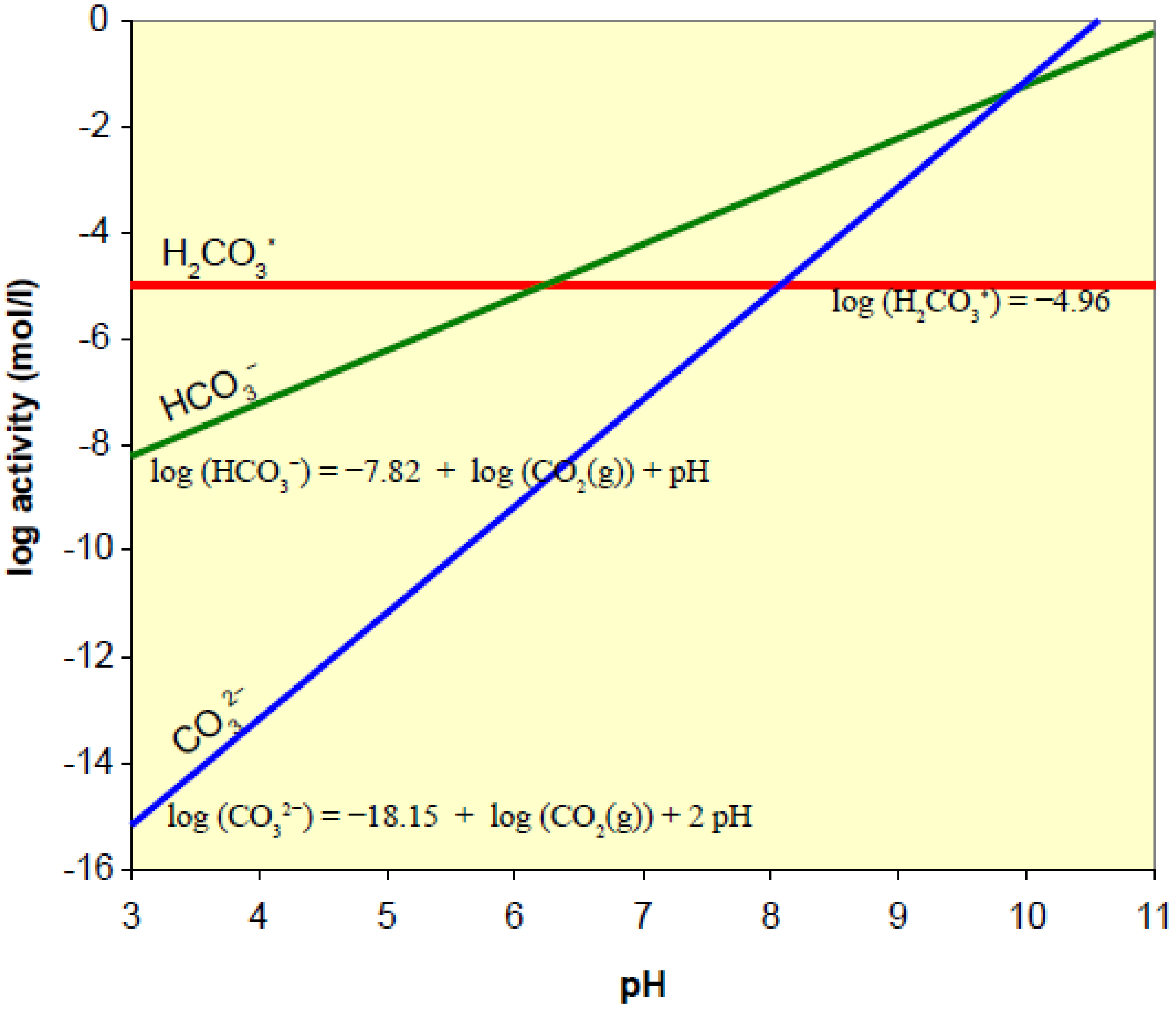
$$\log(CO_3^{2-}) = -18.15 + \log(CO_2(g)) + 2\,pH$$

Answer: [CO2]= **2.61*10-5mol/l**

= 2.61*10-5mol/l *44gmol

=1.15mg/l

CO_2-equilibria



$pCO_2 = 10^{-3.5}$ atm

Problem

1. How much CO_2 can be dissolved in a surface water at pH 6.5?.

   Answer= 1.15mg/l Co_2

2. Calculate the pH of distilled water in equilibrium with the air.

   Answer=5.66

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Calcium in water

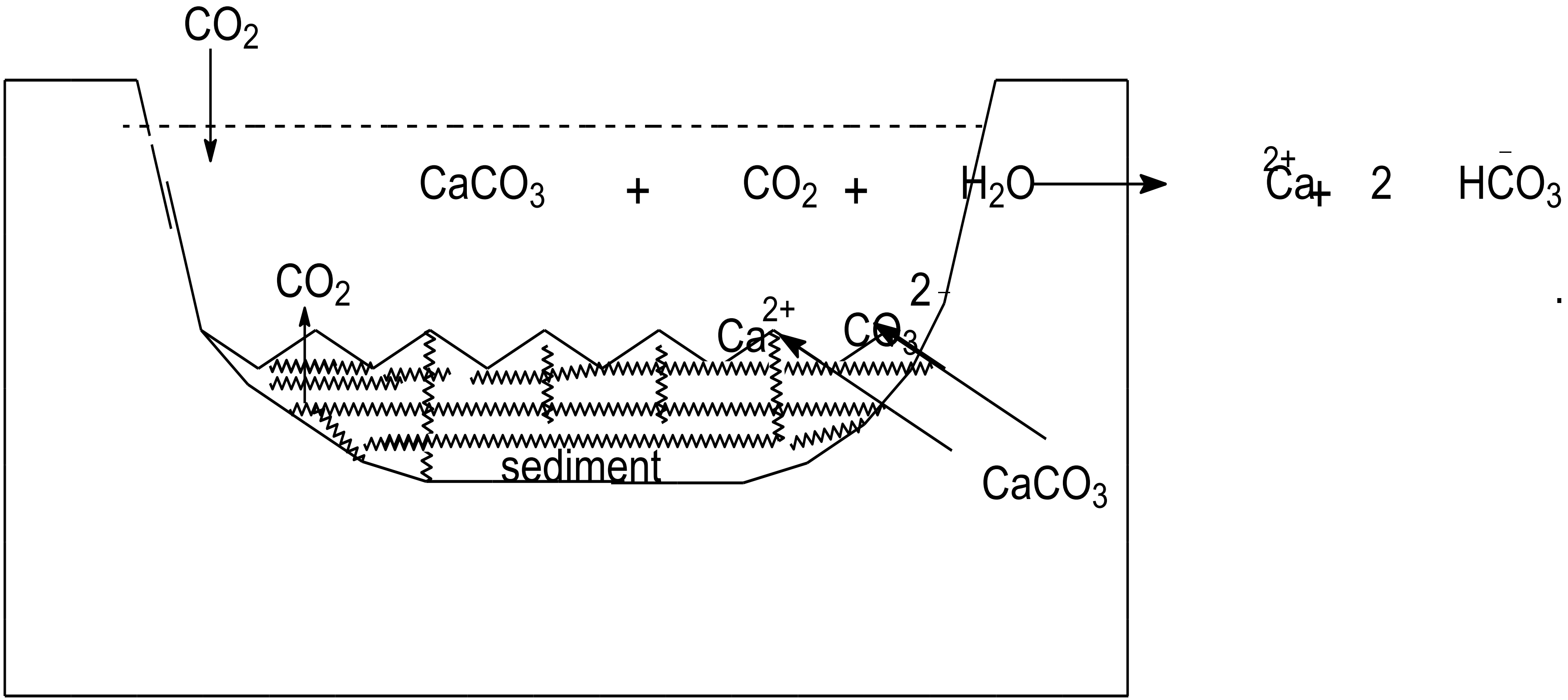
- Has the highest concentration in fresh water
- Simpler chemistry than transition metals
- Reason for water hardness

$$CaCO_3 + CO_2 + H_2O \rightleftharpoons Ca^{2+} + 2HCO_3^-$$

- The extent of dissolved $CaCO_3$ indicates the concentration of CO_2 in water

Where is the source of this CO_2?

Dissolved CO_2 & $CaCO_3$ mineral



$$CaCO_3 + CO_2 + H_2O \longrightarrow Ca^{2+} + 2\ HCO_3^-$$

Carbon dioxide - calcium carbonate equilibri

WATER POLLUTION

Nature and types of Water pollutants

- The relationship between polluted water and disease is a firmly established fact

- Water pollution is imprecise term that revels nothing about either the type of polluting material or its source

- Understanding the sources, transport, interactions, characteristics, and effects of water pollutants is essential for controlling pollutants in an environmentally safe and economically acceptable manner.

Types of pollutants

- There are different types of pollutants in water bodies.

i) Non-conservative or Degradable

- Degradable (non-conservative) pollutants are pollutants (impurities) which eventually decompose into harmless substances or

- which may be removed by treatment methods; that is, certain organic materials and chemicals, domestic sewage, heat, plant nutrients, most bacteria and viruses, certain sediments.

ii) Non-degradable (conservative) pollutants are pollutants (impurities) which persist in the water environment and do not reduce in concentration unless diluted or removed through treatment; that is, certain organic and inorganic chemicals, salts, colloidal suspensions

ii) Pollutants can be Hazardous waterborne pollutants or Radionuclide pollutants

- Hazardous waterborne pollutants: complex forms of deleterious wastes including toxic trace metals, certain inorganic and organic compounds.
- Radionuclide pollutants: materials which have been subjected to a radioactive source.

iii) Based on the source pollutants can be

- **point sources and non-point sources**

Classes of water pollutants

- Oxygen–Demanding Wastes
- Pathogens
- Nutrients
- Salts
- Thermal Pollution
- Heavy Metals
- Pesticides
- Volatile Organic Compounds
- Oxygen, oxidants, and reductants,
- organic pollutants,
- Soaps and Detergents,
- polychlorinated biphenyls.

Oxygen–Demanding Wastes

- Oxygen demanding wastes are substances that oxidize in the receiving body of water, reducing the amount of DO available.
- Oxygen demanding wastes are substances that oxidize in the receiving body of water, reducing the amount of DO available.
- Even naturally occurring organic matter, such as leaves and animal droppings, that find their way into surface water add to the DO depletion.
- Common measures of oxygen demand are COD and BOD

Pathogens

- Contaminated water is responsible for the spread of many communicable diseases.
- May be from human waste contamination.
- Pathogens are disease – producing organisms that grow & multiply within the host.
- Pathogens associated with water include bacteria responsible for cholera, basically dysentery, typhoid, & paratyphoid fever; viruses responsible for infections hepatitis and poliomyelitis; protozoa, which cause amebic dysentery & giardiasis, & helminthes

Nutrients

- Nutrients are chemicals, such as nitrogen, phosphorous, carbon, sulfur, calcium, potassium, ion, manganese, boron, & cobalt, which are essential to the growth of living things.
- In terms of water quality, nutrients can be considered as pollutants when their concentrations are sufficient to allow excessive growth of aquatic plants, particularly algal.
- The attractiveness of the body of water for recreational uses, as a drinking water supply, & as a viable habitat for other living things can be adversely affected.

Nutrients Cont.

- Nutrient enrichment can lead to blooms of algae which eventually die and decompose.
- Their decomposition removes oxygen from the water, potentially leading to levels of DO that are insufficient to sustain normal life forms.
- Algae & decaying organic matter add color, turbidity, odors, and objectionable tastes to water that are difficult to remove & that may greatly reduce its acceptability as a domestic water source.
- The process of nutrient enrichment is called ***eutrophication.***

Salts

- Water naturally accumulates a variety of dissolved solids, or salts
- These salts typically include such actions as sodium, calcium, magnesium, & potassium, & anions such as chloride, sulfate, & bicarbonate.

Major type	Code	Cl-(mg/l)	TDS (mg/l)
Fresh,	F	<150	1500
Fresh brackish	Fb	150-300	
Brackish	B	300-1000	5000
Brackish-salt	BS	1000-10000	
Salt	S	10000-20000	above 5000
Hyper-hyaline	H	>20000	30,000-34,000

Example, Drinking water, has a recommended maximum contaminant level for TDS of 500mg/L.

Thermal Pollution

- A large steam-electric power plant requires a cooling water.
- For example, **nuclear plant** warms about 40 m3 /s of cooling water by 10 °c as it passes through the plant's condenser.
- If that heat is released in to a local river or lake, the resulting **rise in temperature can dramatically affect life** in the vicinity of the thermal plume.

Heavy metals

- Toxic metals includes **aluminum, arsenic, beryllium, bismuth, cadmium, chromium, cobalt, copper, iron, lead, manganese, mercury, nickel, selenium, strontium, thallium, tin, titanium, & zinc.**
- Some of these metals, such as chromium & iron, are essential nutrients in our diets, but in higher doses are extremely toxic.

Pesticide

- Pesticide is used to cover a range of chemicals that kill organisms that humans consider undesirable
- Includes categories of pesticide like insecticides, herbicides, rodenticides, & fungicides.
- 2, 4-D
- DDT
- PCB
  - They are very **persistent and bio-acumulated**

OXYGEN, OXIDANTS, AND REDUCTANTS

- The addition of oxidizable pollutants to streams produces a typical **oxygen sag curve** as shown in Figure below.
- Initially, a well-aerated, unpolluted stream is relatively free of oxidizable material; the oxygen level is high; and the bacterial population is relatively low.
- With the addition of oxidizable pollutant, the oxygen level drops because reaeration cannot keep up with oxygen consumption.
- In the decomposition zone, the bacterial population rises.
- The septic zone is characterized by a high bacterial population and very low oxygen levels.
- The septic zone terminates when the oxidizable pollutant is exhausted, and then the recovery zone begins.
- In the recovery zone, the bacterial population decreases and the dissolved oxygen level increases until the water regains its original condition.

The oxygen sag curve

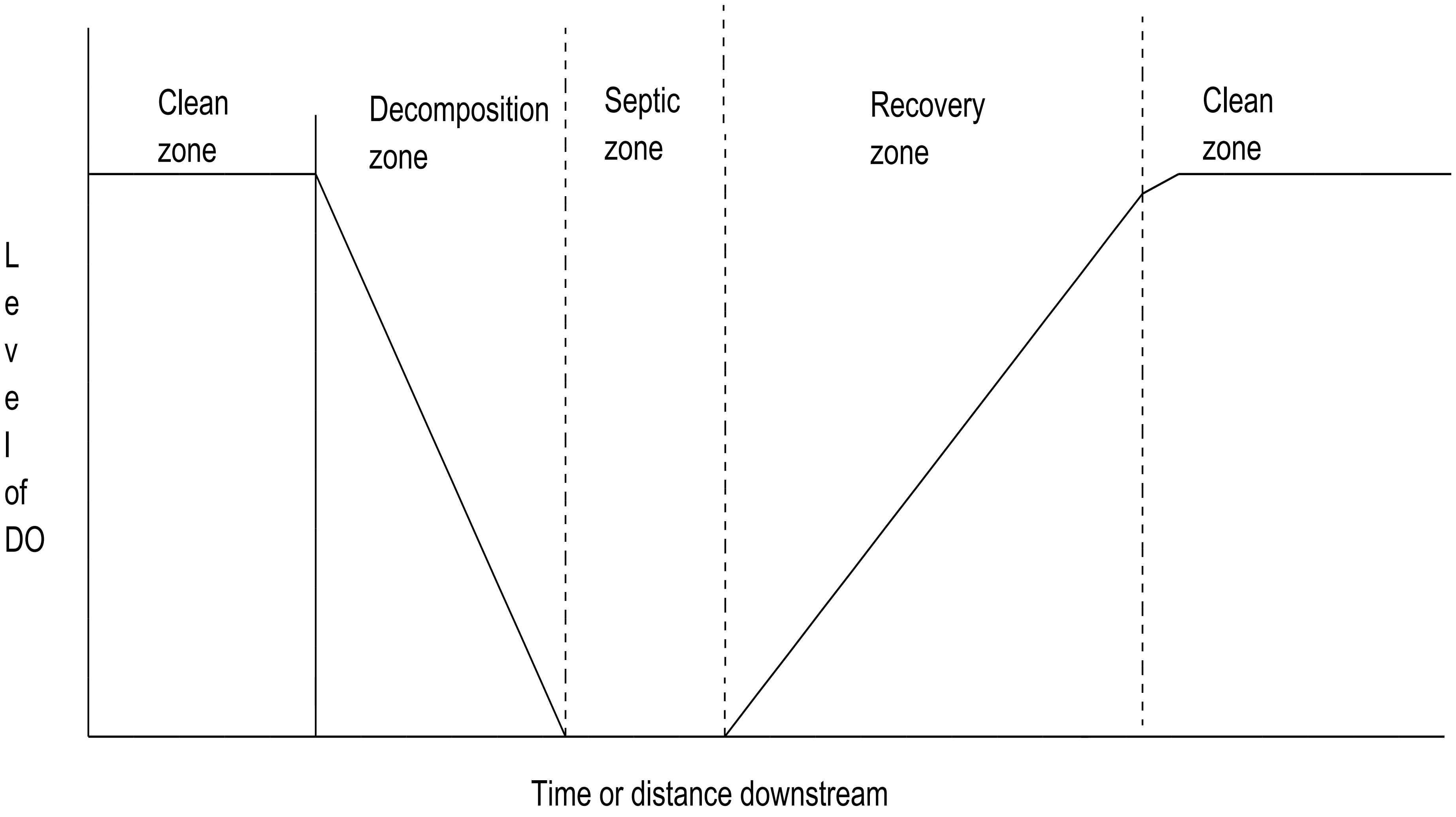


Figure: Oxygen sag curve resulting from the addition of oxidizable pollutant material to a stream.

Organic pollutants

- Sewage from domestic, commercial, food-processing, and industrial sources contains a wide variety of pollutants.
- Some of these pollutants, particularly oxygen-demanding substances such as oil, grease , etc.

CHECK

1. Discuss how thermal stratification of a body of water may affect its chemistry.
2. Relate aquatic life to aquatic chemistry. In so doing, consider the following: autotrophic, producers, heterotrophes, decomposers, eutrophication, dissolved oxygen, biochemical oxygen demand.
3. Discuss the factors that affect the chemistry of water body
4. Discuss the most important unique properties of water. Describe each of the following unique properties of water related to thermal characteristics, transmission of light, surface tension, solvent properties.
5. What are the most important chemical phenomena in water bodies that determine the fate of a toxin in water bodies?

Check---cont'd

6. Indicate how the concentration of dissolved gas in water is determined.

7. What are the processes that supply and deplete oxygen in aquatic systems? Discuss the importance of oxygen and carbon dioxide in aquatic systems? can you site any disadvantage of the mentioned gases in aquatic systems?

8. Derive the formula that would be used to calculate fraction of carbonate ion in water.

9. Which species is predominant in water bodies CO_2, CO_3^{2-} or HCO_3^- ? Justify your reason.

10. What is alkalinity? What is the difference between alkalinity and basicity? How do you measure alkalinity?

Check---cont'd

11. What are the fates of a metal species thrown into water body?
12. Describe the importance of complexation and redox reactions in aquatic systems.
13. How do we detect the tendency of dissolution of a metal atom introduced into a solution that contains another metal ion? Use your own example.
14. How do you describe equilibrium constant for redox reactions?
15. What is pE? How do you measure pE in natural water?
16. What is corrosion? how does that affect the economy?
17. Discuss all the water quality parameters.
18. Relate the oxygen sag curve and bacterial growth pattern on the same curve.

JIMMA UNIVERSITY
COLLEGE OF NATURAL SCIENCE
DEPARTMENT OF CHEMISTRY

❑Environmental chemistry and Toxicology

(Chem 3114).

➢Course to be offered; to Chemistry BSc students

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April, 2020

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❑Chapter 3

❑ATMOSPHERIC CHEMISTRY AND AIR POLUTION

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In this unit we are interested in:

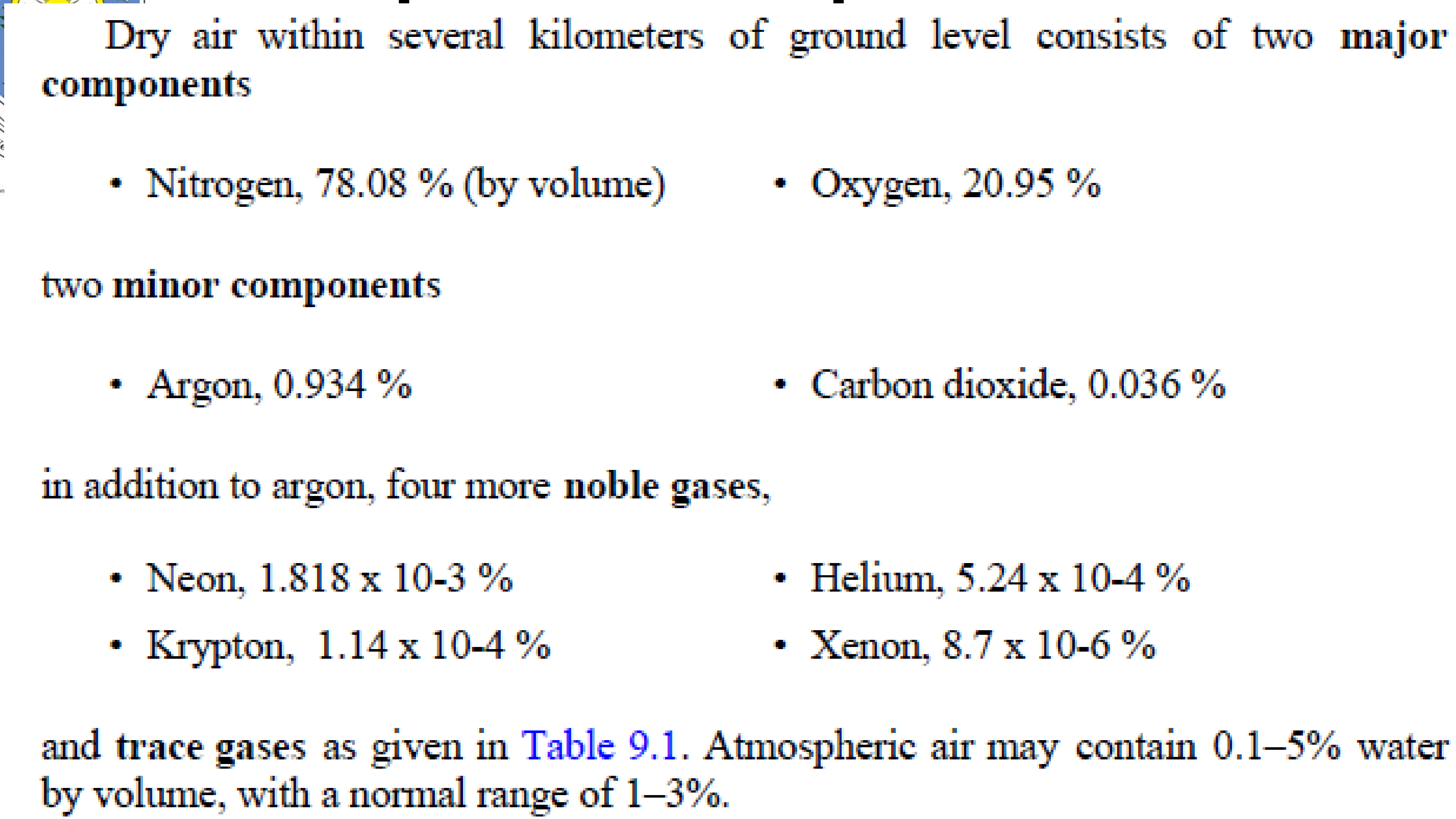
- Importance and physical characteristics of the atmosphere
- Atmospheric chemical reaction
- Air quality
- Nature and classification of air pollutants
  - Gaseous inorganic air pollutants
  - Organic air pollutants
  - Phytochemical smog
  - Chlorofluro compounds and ozone layer depletion
- Green house gases and global warming

Definitions and composition

- **Atmosphere** is a thin layer of mixed gases covering the earth‘s surface.

- **Atmospheric science** deals with the movement of air masses in the atmosphere, atmospheric heat balance, and atmospheric chemical composition and reactions.

Atmospheric Composition



Dry air within several kilometers of ground level consists of two **major components**

- Nitrogen, 78.08 % (by volume)
- Oxygen, 20.95 %

two **minor components**

- Argon, 0.934 %
- Carbon dioxide, 0.036 %

in addition to argon, four more **noble gases**,

- Neon, 1.818 x 10-3 %
- Helium, 5.24 x 10-4 %
- Krypton, 1.14 x 10-4 %
- Xenon, 8.7 x 10-6 %

and **trace gases** as given in Table 9.1. Atmospheric air may contain 0.1–5% water by volume, with a normal range of 1–3%.

- ❑**Trace level gases at levels below 0.002%, including methane, nitrous oxide, hydrogen, sulfur dioxide, ozone, nitrogen dioxide, ammonia, and carbon monoxide.**

Gaseous Oxides in the Atmosphere

Oxides of **carbon**, **sulfur(Sox)**, **and** **nitrogen** (NOx) are important constituents of the atmosphere and are pollutants at higher levels.

- H_2SO_4 and HNO_3 are the predominant contributor to **acid precipitation**
- Of these, **carbon dioxide, CO_2**, is the most abundant. It is a natural atmospheric constituent, and it is **required for plant growth.**
- However, the **level of carbon dioxide** in the atmosphere, now at about 360 ppm by volume, is **increasing** by about 1 ppm per year.
- This increase in atmospheric CO_2 may well **cause** general atmospheric warming; the —**greenhouse effect**, with potentially very serious consequences for the global atmosphere and for life on earth. Though not a global threat, carbon monoxide (CO) can be a **serious health threat** because it prevents **blood from transporting** oxygen to body tissues.

Hydrocarbons and Photochemical Smog

□ The **most abundant** hydrocarbon in the atmosphere is **methane, CH_4**, released from underground sources as natural gas and produced by the **fermentation of organic matter**.

□ Methane is produced **by diffuse sources**, so that its participation in the formation of pollutant photochemical reaction products is minimal.

□ The most significant atmospheric pollutant hydrocarbons are the **reactive ones produced as automobile exhaust emissions in the presence of NO,** under conditions of temperature inversion

Nitrous oxide

- The two most serious nitrogen oxide air pollutants are nitric oxide (NO) and nitrogen dioxide (NO2) collectively denoted as —NOx.
- These tend to enter the atmosphere as NO, and
- photochemical processes in the atmosphere can convert NO to NO2. Further reactions can result in the formation of corrosive nitrate salts or nitric acid, HNO_3.
- Nitrous oxide (N_2O) is an important greenhouse gas, ranking fourth behind **CO_2, CH_4, and CFC- 12**
- 4.8 * Ozone in its ability to change the Earth’s infrared radiative budget.
- The stratosphere is the principal sink for N_2O.

Ozone (O_3)

- Ozone is an important atmospheric gas for several reasons.
- Its absorption of solar ultraviolet (UV) radiation in the stratosphere,
- Reductions in stratospheric ozone are linked to increasing incidence of skin cancer.
- absorption of UV radiation by O_3 causes heating and essentially determines the vertical temperature profile in the stratosphere.
- Ozone participates in many chemical reactions.

cont.

- **The production of stratospheric ozone** begins with the dissociation of molecular oxygen by UV radiation into atomic oxygen: O_2 + sunlight → O + O.
- In the presence of N_2 or O_2, here represented by M, atomic and molecular oxygen combine to form ozone:

$$O + O_2 + M \longrightarrow O_3 + M.$$

- The **destruction of stratospheric O_3 occurs** by several pathways.
- The most direct is the reaction $O + O_3 \rightarrow 2\,O_2$, which is fairly slow, but several catalytic reactions of the form
- $$X + O_3 \longrightarrow XO + O_2$$
  $$\underline{XO + O \longrightarrow X + O_2}$$
- Net: $O_3 + O \rightarrow 2O_2$
- can speed the destruction of O_3, where X is the catalyst. The most important catalysts are hydrogen (H), the hydroxyl radical (OH), nitric oxide (NO), and chlorine (Cl).

Particulate Matter(PM)

- **Particles** ranging from aggregates of a **few molecules** to **pieces of dust readily visible to the naked eye** are commonly found in the atmosphere.
- Smaller particles are in general the **most harmful** because they have a **greater tendency to scatter light** and are the **most respirable** (tendency to be inhaled into the lungs).
- Much of the **mineral particulate matter** in a polluted atmosphere is in the form of **oxides** and other compounds produced during the combustion of high-ash fossil fuel **(fly ash).**
- This smaller particles causes **damage to human health, plants, and visibility.**

Importance of the atmosphere

- The atmosphere is a **protective blanket** which nurtures **life on the Earth** and protects it from the **hostile environment of outer space.**
- In its essential role as a protective shield, the atmosphere absorbs most of the cosmic rays from outer space and protects organisms from their effects. otherwise be very harmful to living organisms
- The atmosphere is the source of **carbon dioxide for plant photosynthesis** and of oxygen for **respiration**.
- It provides the **nitrogen that nitrogen-fixing bacteria** and ammonia-manufacturing plants use to produce chemically-bound nitrogen, an essential component of life molecules.
- As a **basic part of the hydrologic cycle,** the atmosphere transports water from the oceans to land, thus acting as the condenser in a vast solar-powered still.
- Furthermore, because it reabsorbs much of the infrared radiation by which **absorbed solar energy is re-emitted to space**, the atmosphere **stabilizes the earth's temperature**, preventing the tremendous **temperature extremes** that occur on planets and moons lacking substantial atmospheres.

Cont.,

- Unfortunately, the atmosphere also has been used as a **dumping ground for many pollutant** materials ranging from **sulfur dioxide to refrigerant Freon** a practice which causes **damage to vegetation and materials, shortens human life, and alters** the characteristics of the atmosphere itself.

3.1 Stratification of the Atmosphere

- The atmosphere is **stratified on the basis of the temperature/density relationships** resulting from interactions between physical and photochemical (light-induced chemical phenomena) processes in air.

1. **Troposphere** extending in altitude from the earth‘s surface to approximately 11 km: 15°C at sea level to an average of -56°C at its upper boundary.

- The lowest layer of the atmosphere extending from sea level to an altitude of 10-16 km
- characterized by a generally homogeneous composition of major gases other than water and **decreasing temperature with increasing altitude** from the heat-radiating surface of the earth.

Troposphere Cont.,

- The homogeneous composition of the troposphere results from constant mixing by circulating air masses.

- However, the water vapor content of the troposphere is extremely variable because of cloud formation, precipitation, and evaporation of water from terrestrial water bodies.

- The very cold temperature of the **tropopause** layer at the top of the troposphere serves as a barrier that causes water vapor to condense to ice , as a result helps as a reservoir for hydrogen in the earths atmospheres

Stratification Cont.,

2. Stratosphere from about 11 km to approximately 50 km.

- The average temperature of the stratosphere increases from -56°C at its boundary with the troposphere to –2°C at its upper boundary.
- temperature rises to a maximum of about -2°C with increasing altitude.
- The reason for this increase is absorption of solar ultraviolet energy by ozone (O3) in the stratosphere.
- This phenomenon is due to the presence of ozone, O3, which may reach a level of around 10 ppm by volume in the mid-range of the stratosphere.

Stratification Cont.,

3. Mesosphere (50-85km)

- The absence of high levels of radiation-absorbing species in the **mesosphere** immediately above the stratosphere results in a further temperature decrease to about –92°C at an altitude around 85 km.

4). Thermosphere (85km -500km

- The **thermosphere** is the **fourth layer** of the Earth's atmosphere and is located above the mesosphere.
- The **air is really thin in** the thermosphere.
- A small change in **energy can cause** a large **change in temperature**. That's why the temperature is very sensitive to solar activity.
- When the sun is active, the thermosphere can heat up to 1,500° C or higher!
- Extending to the far outer reaches of the atmosphere is the **thermosphere**, in which the highly rarified gas reaches temperatures as high as 1200°C by the absorption of very **energetic radiation** of wavelengths less than approximately 200 nm by gas species in this region.

thermosphere Cont.,

- The Earth's thermosphere also includes the region of the atmosphere called the **ionosphere.**
- The ionosphere is a region of the atmosphere that is filled with charged particles.
- The **high temperatures in the thermosphere can cause molecules to ionize.**
- **This is why an ionosphere and thermosphere can overlap.**

Exosphere

- The upper regions of the mesosphere and higher define a region called the exosphere from which molecules and ions can completely escape the atmosphere.
- Very high up, the Earth's atmosphere becomes very thin.
- The region where atoms and molecules escape into space is referred to as the **exosphere.**
- The exosphere is on top of the thermosphere.
- The atmosphere merges into space in the extremely thin **exosphere**.
- This is the upper limit of our atmosphere.

Figure 3.1 Stratification of the atmosphere

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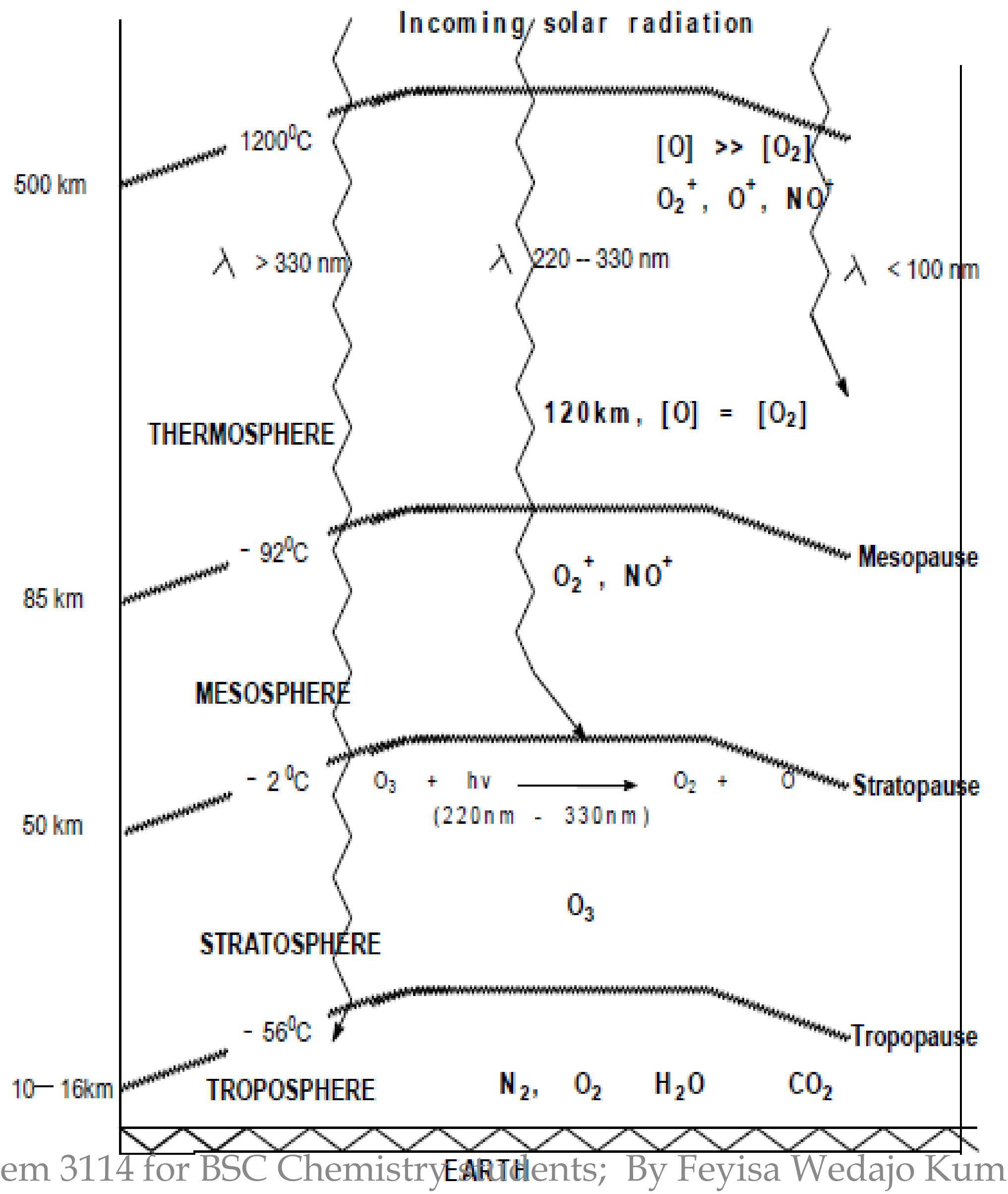

Cont.,

- Incoming solar energy is largely in the visible region of the spectrum.
- The shorter wavelength **blue solar light is scattered** relatively more strongly by molecules and particles in the upper atmosphere, which is why the **sky is blue as it is viewed by scattered light.**
- Similarly, **light that has been transmitted through scattering atmospheres appears red, particularly around sunset and sunrise, and under circumstances** in which the atmosphere contains a high level of particles.

3.2 Variation of Pressure and Density with Altitude

- The density of the atmosphere decreases sharply with increasing altitude as a consequence of the gas laws and gravity.
- Atmosphere is tissue-thin protective layer as compared to the earths diameter.
- More than 99% of the total mass of the atmosphere is found within approximately 30 km of the Earth‘s surface.
- mass of atmosphere is approximately 5.14 x 10^{15} metric tons, it is still about one millionth of the Earth‘s total mass.

Cont.,

- The atmospheric pressure decreases as an approximately exponential function of altitude.
- At a constant absolute temperature, T, the pressure at any given height, Ph, is given in the exponential form:

$$Ph = P_o e^{-Mgh/RT}$$

- Where Po pressure at zero altitude (sea level); M average molar mass of air (28.97 g/ mol in the troposphere); g is acceleration due to gravity and h is the altitude.

Cont.,

- The characteristics of the atmosphere vary widely with altitude, time (season), location (latitude), and even solar activity.
- At very high altitudes, normally reactive species such as atomic oxygen, O, **persist for long periods** of time.
- That occurs **because the pressure is very low at these altitudes** such that the distance traveled by a reactive species.

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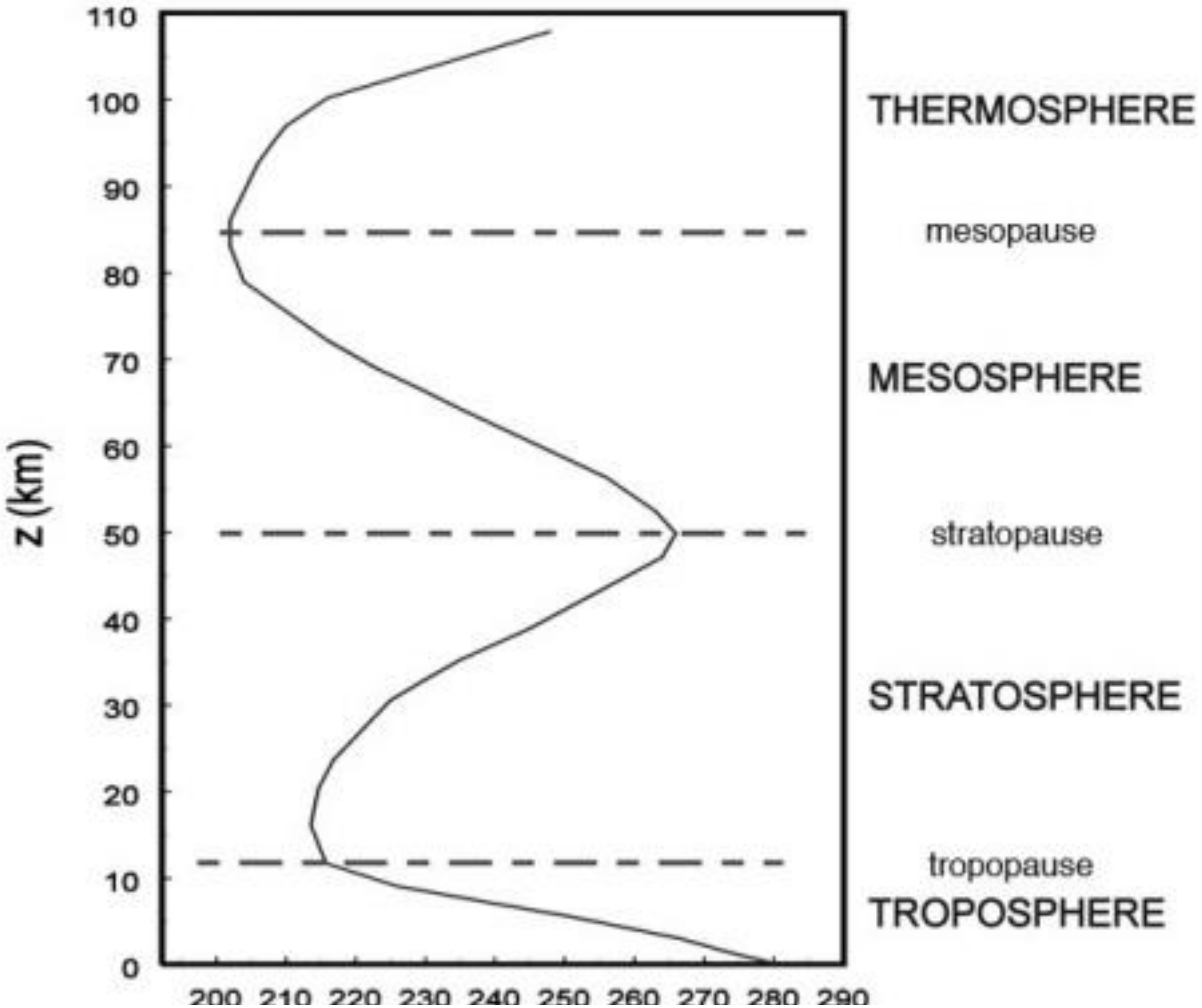
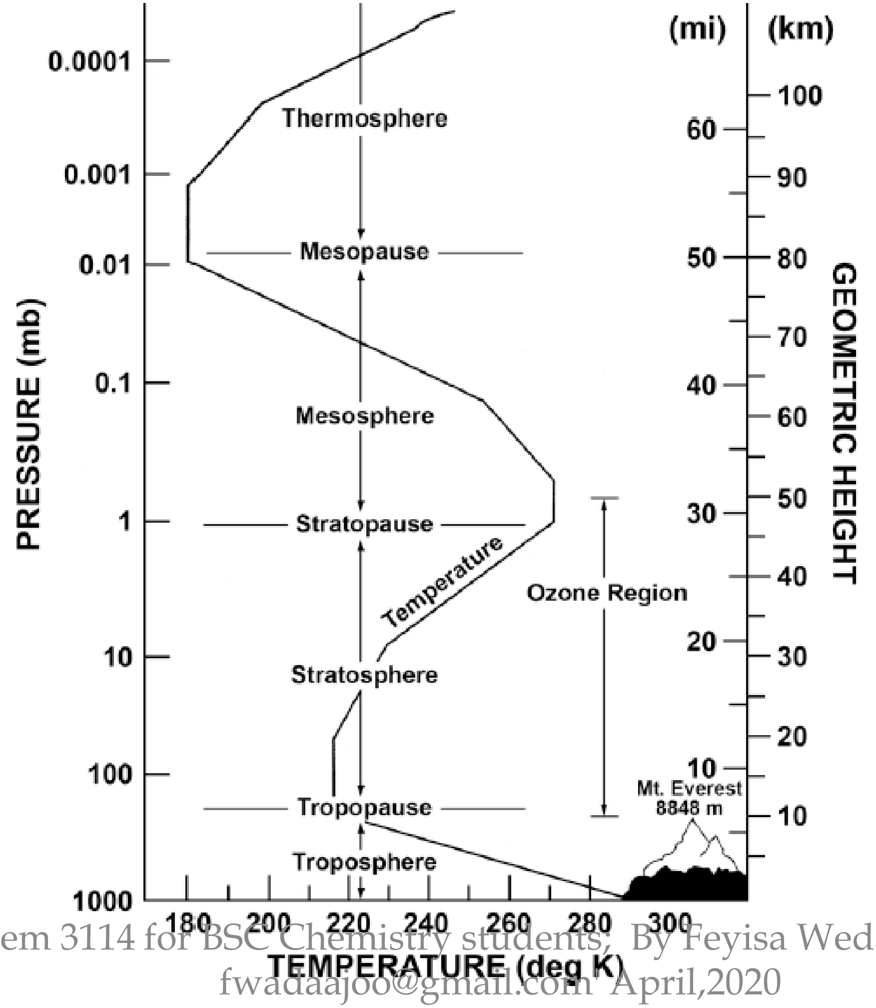


Figure 3.1: Vertical temperature profile for the 'US standard atmosphere' at 40° *N* in December.

Figure 3. Vertical temperature structure of the atmosphere extending from the surface of the Earth to approximately 110-km altitude as given in the *U.S. Standard Atmosphere, 1976*. The principal layers defined by this temperature structure and the interfaces between them are labeled. As indicated, ozone is found principally in the stratosphere. Two vertical coordinates are given: pressure on the left in millibars (1 mb = 100 Pascal) and geometric altitude on the right (km).



3.3. Atmospheric chemical reactions

- ***Atmospheric chemistry involves the unpolluted atmosphere, highly polluted atmospheres, and a wide range of gradations in between.***
- Many chemical reactions that require a third body to absorb excess energy occur very slowly in the upper atmosphere where there is a sparse concentration of third bodies, but occur readily in a container whose walls effectively absorb energy.

Gaseous atmospheric chemical species fall into the following classifications:

- **Inorganic oxides (CO, CO_2, NO_2, SO_2),**
- **Oxidants (O_3, H_2O_2, HO)**
- **Radical, HO_2• radical, ROO• radicals, NO_3),**
- **Reductants (CO, SO_2, H_2S),**
- **Organics (also reductants; in the unpolluted atmosphere, CH_4 is the predominant organic species, whereas alkanes, alkenes, and aryl compounds are common around sources of organic pollution),**
- **Oxidized organic species (carbonyls, nitrates),**
- **Photo chemically active species (NO_2, formaldehyde),**
- **Acids (H_2SO_4), bases (NH_3), salts (NH_4HSO_4,), and**
- **Unstable reactive species (electronically excited NO_2, HO• radical).**

Cont,

- **Solid and liquid particles** in atmospheric aerosols and clouds play a strong role in atmospheric chemistry as sources and sinks for gas-phase species, **as sites for surface reactions** (solid particles), and as bodies for aqueous-phase reactions (liquid droplets).

3.4. Photochemical Reactions /Processes/

- The absorption by chemical species of light (UV) radiation from the sun, can bring about reactions, called **photochemical reactions**.
- photochemical reactions can ocour, even in the absence of a chemical catalyst.
- Nitrogen dioxide, NO_2, is one of the most photochemically active species found in a polluted atmosphere and is an essential participant in the smog-formation process.
- NO_2 may absorb light of energy hv, producing an **electronically excited molecule**

$$NO_2 + h\nu \rightarrow NO_2^*$$

Cont,

- Electronically excited molecules are **one of the three relatively reactive and unstable species** that are encountered in the atmosphere and are strongly involved with atmospheric chemical processes.
- The other two species are atoms or molecular fragments with unshared electrons, called **free radicals,** and **ions** consisting of electrically-charged atoms or molecular fragments.
- Reactions that occur following absorption of a photon of light to produce an electronically excited species are largely determined by the way in which the excited species loses its excess energy.

This phytochemical reaction may occur by one of the following processes:

1. **Physical quenching** - loss of energy to another molecule or atom (M) followed by dissipation of the energy as heat: $O2* + M \rightarrow O2 + M$(higher translational energy)
2. **Dissociation** of the excited molecule (the process responsible for the predominance of atomic oxygen in the upper atmosphere): $O2* \rightarrow O + O \bullet$
3. **Direct reaction** with another species: $O2* + O3 \rightarrow 2O2 + O \bullet$

- **Luminescence** consisting of loss of energy by the emission of electromagnetic radiation $NO2* \rightarrow NO2 + hv$

- If the re-emission of light is almost instantaneous (immediate, rapid, sudden) luminescence is called **fluorescence**, and
- if it is significantly delayed, the phenomenon is **phosphorescence**.

cont.,

4. **Chemiluminescence** is said to occur when the excited species (such as NO2* below) is formed by a chemical process:

$$O_3 + NO \rightarrow NO_2^* + O_2 \text{(higher energy)}$$

5. **Intermolecular energy transfer** in which an excited species transfers energy to another species which then becomes excited:

$$O_2^* + Na \rightarrow O_2 + Na^*$$

A subsequent reaction by the second species is called a **photosensitized** reaction.

Cont.,

6. **Intramolecular transfer** in which energy is transferred within a molecule

- XY* → XY†(where † denotes another excited state of the same molecule)

7. **Photoionization** through loss of an electron

- $N_2^* \rightarrow N_2^+ + e^-$

3.5.1 Reactions in Troposphere

- The main reactions in troposphere takes place are:

I. **Acid – base reactions**,

II. Redox reaction,

III. **Complexation reaction**,

IV. Precipitation and others.

V. **Photochemical smog formation**,

VI. Acid rain formation,

Cont.,

- The atmosphere is normally at least slightly acidic because of the presence of CO_2,SO_2,H_2S, etc, which dissolves in atmospheric water droplets and dissociates slightly.

$$CO_2(g) \rightarrow CO_2(aq)$$

$$CO_2(aq) + H_2O \rightarrow H^+ + HCO_3^-$$

$$SO_2(g) + H_2O \rightarrow H^+ + HSO_3^-$$

- HNO_3 and H_2SO_4 formed by the atmospheric oxidation of N oxides, SO_2, and H_2S are much more important because they lead to the formation of damaging acid rain.

- Particulate calcium oxide, hydroxide, and carbonate can get into the atmosphere from ash and ground rock and can react as

$$Ca(OH)_2(s) + H_2SO_4(aq) \rightarrow CaSO_4(s) + 2H_2O$$

Cont.,

- The most important basic species in the atmosphere is gas-phase ammonia, NH_3. The major source of atmospheric ammonia is from biodegradation of nitrogen containing biological matter and from bacterial reduction of nitrate:

$$NO_3^-(aq) + 2\{CH_2O\}(\textit{biomass}) + H^+ \rightarrow NH_3(g) + 2CO_2 + H_2O$$

- NH_3 plays a strong role in neutralizing atmospheric acids:
- $NH_3\ (aq) + HNO_3\ (aq) \rightarrow NH_4NO_3\ (aq)$
- $NH_3\ (aq) + H_2SO_4\ (aq) \rightarrow NH_4HSO_4\ (aq)$
- They serve to neutralize acidic constituents of the atmosphere, and produce relatively corrosive ammonium salts.

3.5.2 Reactions in Stratosphere

❑Ozone layer formation and depletion

I. Ozone formation and depletion in Stratosphere

ozone, O_3, serves as a shield to absorb harmful ultraviolet radiation in the stratosphere, protecting living beings on the earth

- The two reactions by which stratospheric ozone is ***produced (formed)*** are:

$O_2 + hv \rightarrow O + O$ ($\lambda < 242.4$ nm)

$O + O_2 + M \rightarrow O_3 + M$ (energy-absorbing N_2 or O_2)

- And it is **depleted (destroyed)** by photo dissociation,

$$O_3 + hv \rightarrow O_2 + O \ (\lambda < 325 \text{ nm})$$

and a series of reactions from which the net result is the following:

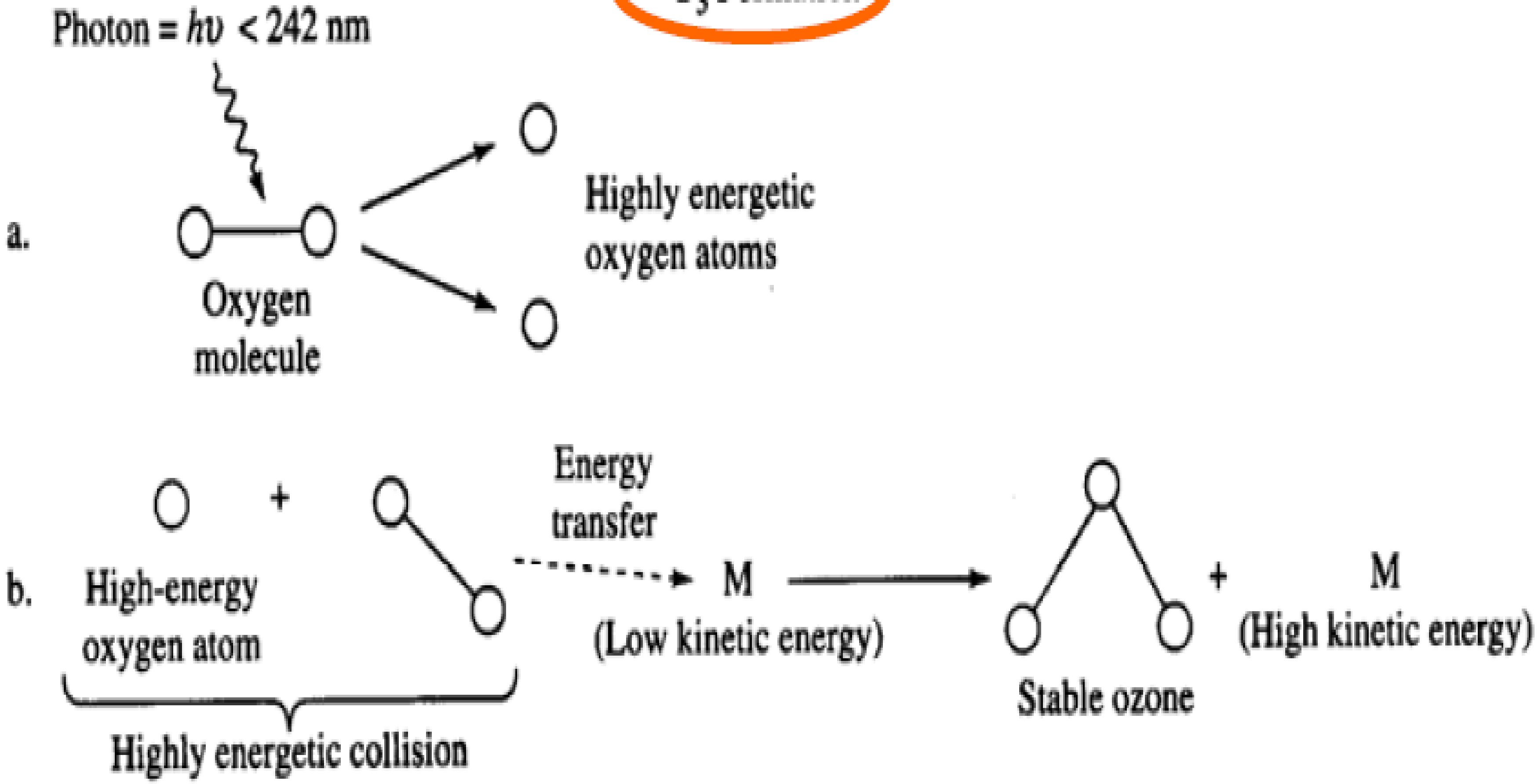
$O + O_3 \rightarrow 2O_2$

- ❖Approximately, a total of about 350,000 metric tons of ozone are formed and destroyed daily.

Ozone formation and destruction in the stratosphere

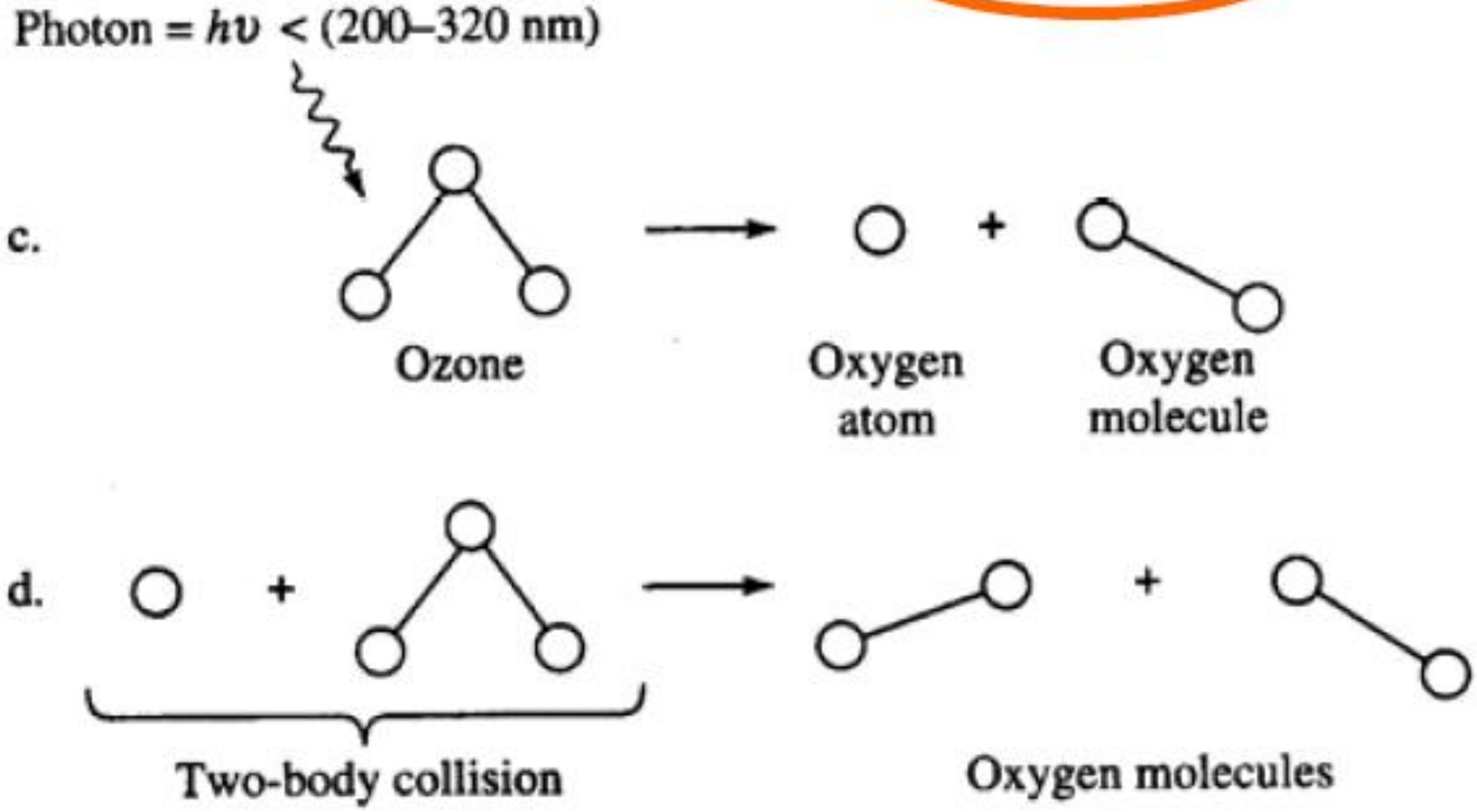
- **Chapman theory** describes how sunlight converts the various forms of oxygen from one to another.
- O3 depletion: when sum of ozone over height is lower than 2/3 of the normal value.

O_3 Formation

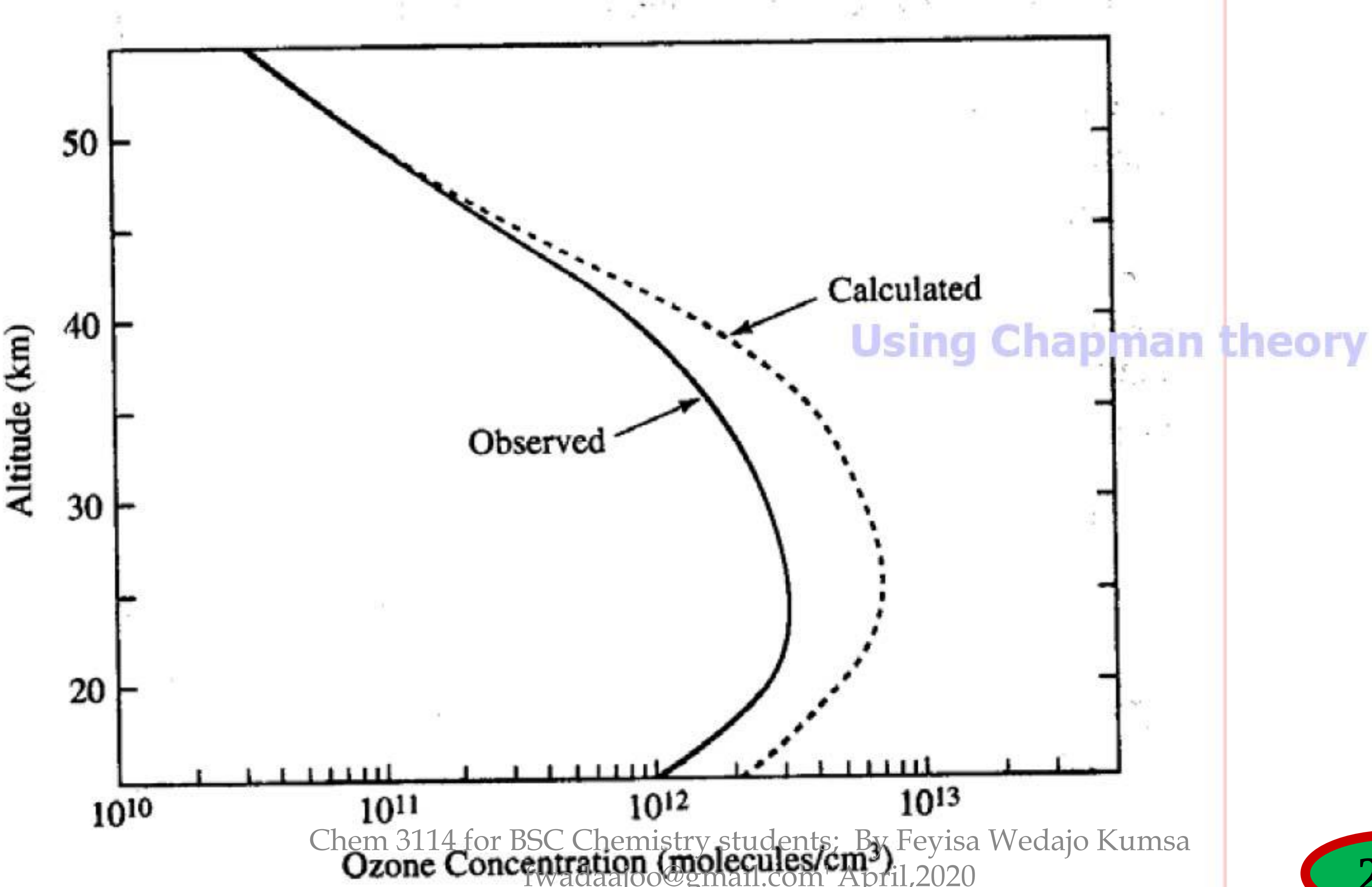


(M is a third body, for example N_2, O_2)

O_3 Destruction



Prediction by Chapman theory vs. observation



There must be other O_3 destruction pathways → Catalytic ozone destruction

$$X + O_3 = XO + O_2$$

$$XO + O = X + O_2$$

Net reaction $$O + O_3 = 2\,O_2$$

where X, a third component, acts as a catalyst

The **important catalysts** for stratospheric O_3 destruction:

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- Hydroxy radical (OH)

$$\left.\begin{array}{c} {}^{\cdot}\mathrm{OH} + \mathrm{O3} = \mathrm{HO2}^{\cdot} + \mathrm{O2} \\ \mathrm{HO2}^{\cdot} + \mathrm{O} = {}^{\cdot}\mathrm{OH} + \mathrm{O2} \\ \text{Net: } \mathrm{O} + \mathrm{O3} = 2\ \mathrm{O2} \end{array}\right\} \text{HOx cycle}$$

- Chlorine and bromine (Cl and Br)

$$\left.\begin{array}{c} \mathrm{Cl}^{\cdot} + \mathrm{O3} = \mathrm{ClO}^{\cdot} + \mathrm{O2} \\ \mathrm{ClO}^{\cdot} + \mathrm{O} = \mathrm{Cl}^{\cdot} + \mathrm{O2} \\ \text{Net: } \mathrm{O} + \mathrm{O3} = 2\ \mathrm{O2} \end{array}\right\} \text{ClOx cycle}$$

- Nitric oxide (NO)

$$\left.\begin{array}{c} \mathrm{NO} + \mathrm{O3} = \mathrm{NO2} + \mathrm{O2} \\ \mathrm{NO2} + \mathrm{O} = \mathrm{NO} + \mathrm{O2} \\ \text{Net: } \mathrm{O} + \mathrm{O3} = 2\ \mathrm{O2} \end{array}\right\} \text{NOx cycle}$$

Cont.,

- The major cause in ozone depletion consists of chlorofluorocarbon (CFC) compounds, commonly known as —Freons.
- These volatile compounds have been used and released to a very large extent in recent decades.
- The major use associated with CFCs is as refrigerant fluids.
- Other applications have included solvents, aerosol propellants, and blowing agents in the fabrication of foam plastics.

Cont.,

- In the stratosphere, the photochemical dissociation of CFCs by intense ultraviolet radiation yields chlorine atoms

$$CF_2Cl_2 + h\nu \rightarrow Cl\bullet + CClF_2\bullet$$

$$Cl\bullet + O3 \rightarrow ClO\bullet + O_2$$

$$ClO\bullet + O \rightarrow Cl\bullet + O_2$$

- The net effect of these reactions is catalysis of the destruction of several thousand molecules of O_3 for each Cl atom produced.
- Because of their widespread use and persistency, the two CFCs of most concern in ozone destruction are CFC-11 and CFC-12, $CFCl_3$ and CF_2Cl_2 respectively.
- CFC have lifetimes of the order of 100 years.

- The most prominent instance of ozone layer destruction is the so-called ***"Antarctic ozone hole"***

Antarctic O3 hole

- The most prominent instance of ozone layer destruction is the so-called ***“Antarctic ozone hole”***.

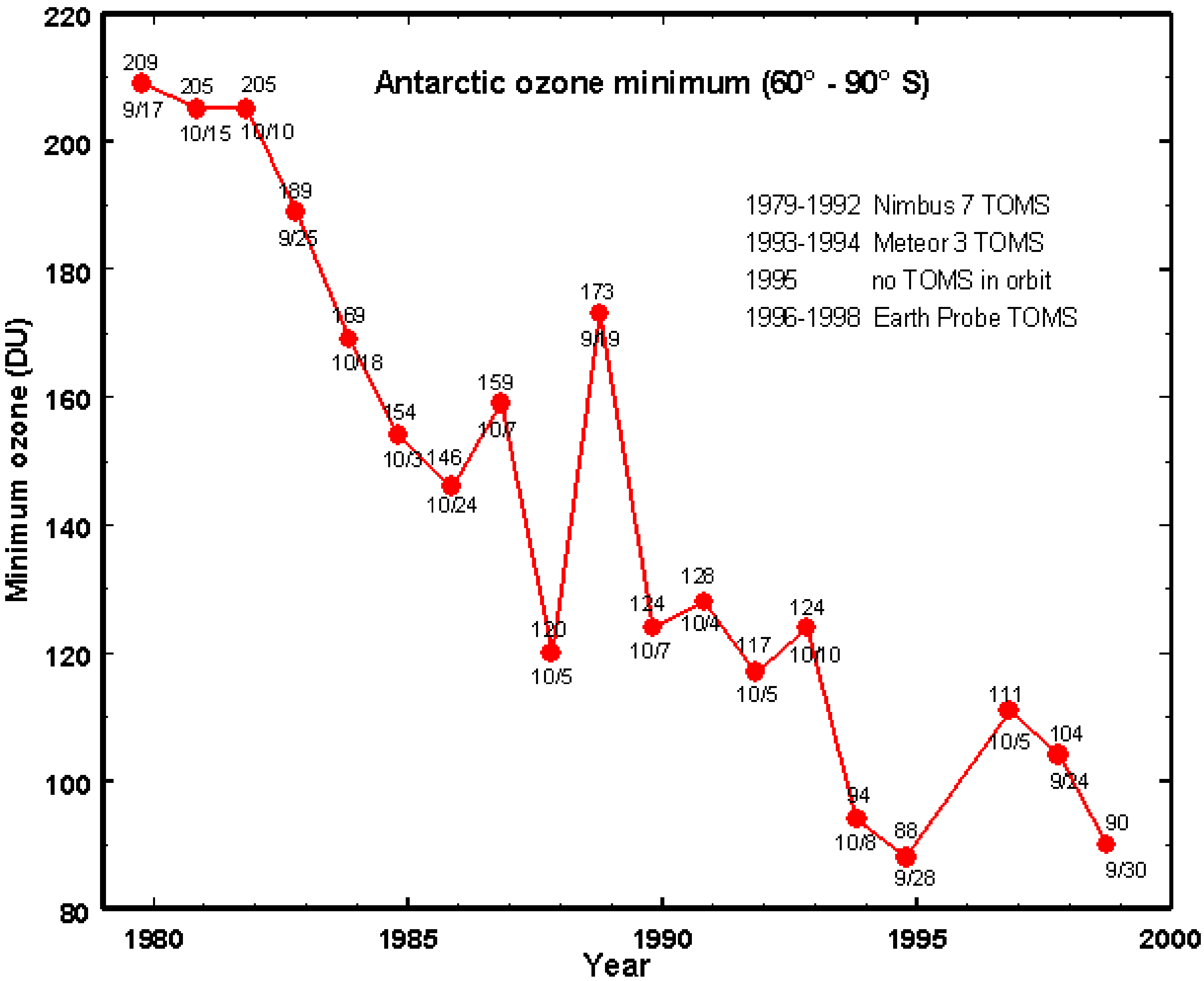
- This phenomenon is manifested by the appearance during the Antarctic‘s late winter and early spring of severely depleted stratospheric ozone (up to 50%) over the polar region.

- ✓The reasons why this occurs are related to the normal effect of NO_2 in limiting Cl-atom-catalyzed destruction of ozone by combining with ClO,

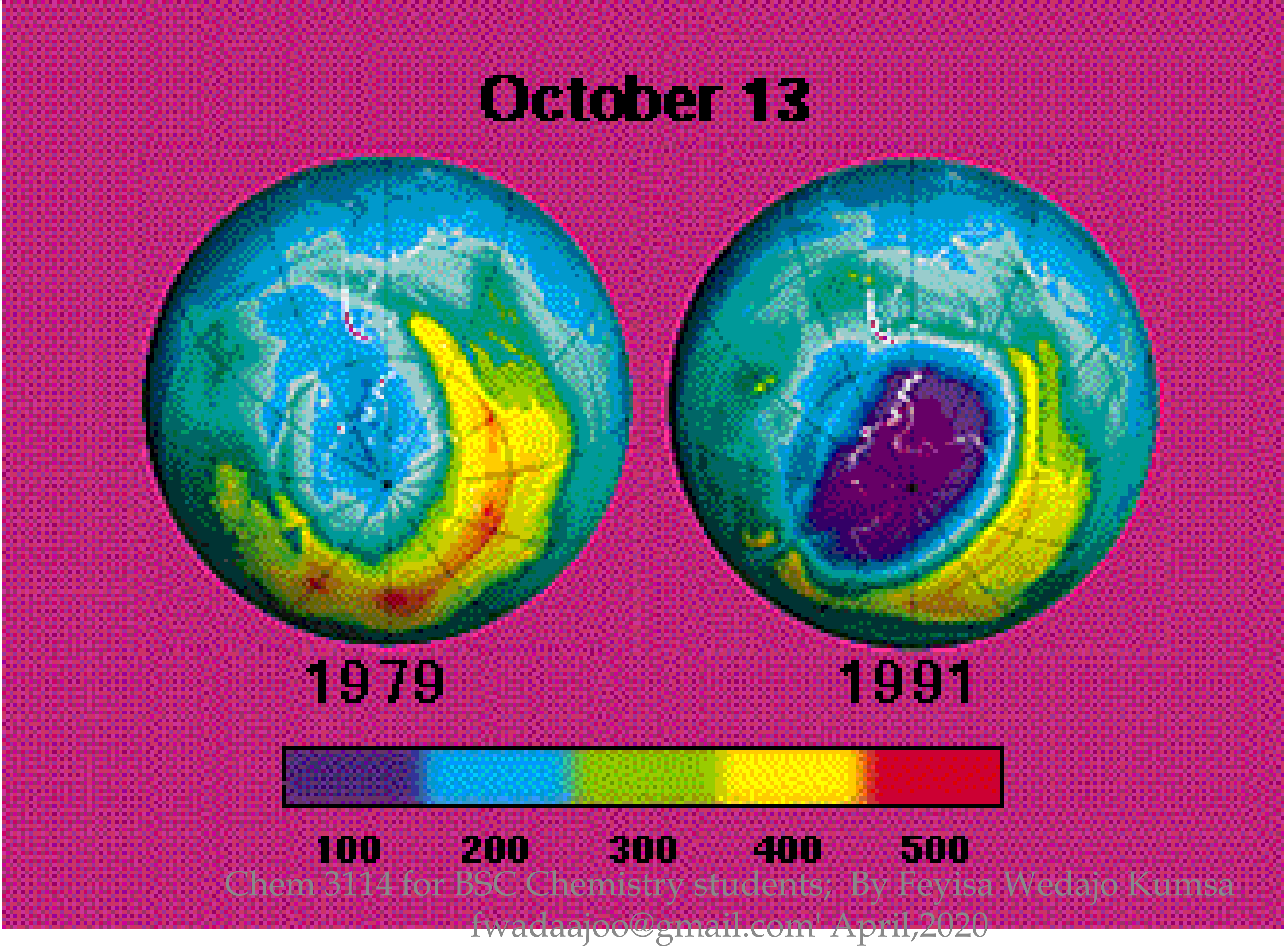
- ❖ $ClO + \mathbf{NO_2} \rightarrow \mathbf{ClONO_2}$

The discovery of the ozone hole

- The **British Antarctic Survey has been monitoring**, for many years, the total column ozone levels at its base at Halley Bay in the Antarctica.
- **Monitoring data indicate that column ozone levels have been decreasing since 1977.**
- This observation was later confirmed by satellite data (**TOMS-Total Ozone Mapping Spectrometer)**
  - Initially satellite data were assumed to be wrong with values lower than **190DU**


Antarctic ozone minimum (60° - 90° S)
Minimum ozone (DU)
220
200
180
160
140
120
100
80
Year
1980
1985
1990
1995
2000
1979-1992 Nimbus 7 TOMS
1993-1994 Meteor 3 TOMS
1995 no TOMS in orbit
1996-1998 Earth Probe TOMS
209
9/17
205
10/15
205
10/10
189
9/25
169
10/18
154
10/3
146
10/24
159
10/7
120
10/5
173
9/19
124
10/7
128
10/4
117
10/5
124
10/10
94
10/8
88
9/28
111
10/5
104
9/24
90
9/30

October ozone hole over Antarctic



Polar vortex

- The polar vortex is a persistent large-scale **cyclonic circulation pattern** in the middle and upper troposphere and the stratosphere, centered generally in the polar regions of each hemisphere.
- The polar vortex is not a surface pattern. It tends to be well expressed at upper levels of the atmosphere (> 5 km).

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Polar Stratospheric Clouds (PSCs)

- PSCs first form as nitric acid trihydrate ($HNO3 \cdot 3H2O$) once temperature drops to 195K.
- As the temperature gets colder, larger droplets of water-ice with nitric acid dissolved in them can form.
- PSCs occur at heights of 15-20km.

Cont.,

- In the polar regions, particularly Antarctica, NOx gases are removed along with water by freezing in polar stratospheric clouds(PSC) at temperatures below -70°C as compounds such as $ClONO_2$ and $HNO_3•3H_2O$.
- During the Antarctic winter, HOCl and Cl2 are generated and accumulate at the surfaces of the solid cloud particles by the reactions,
  - ✓$ClONO_2 + H_2O \rightarrow HOCl + HNO_3$
  - ✓$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3$
- ❖HCl comes primarily from the reaction of stratospheric methane, CH4, with Cl• atoms produced from chlorofluorocarbons

Cont.,

- The result of these processes is that over the winter months photoreactive $Cl2$ and $HOCl$ accumulate in the Antarctic stratospheric region in the absence of sunlight then undergo a burst of photochemical activity when spring arrives as shown by the following reactions:
- $HOCl + h\nu \rightarrow HO\bullet + Cl\bullet$
- $Cl2 + h\nu \rightarrow Cl\bullet + Cl\bullet$
- The Cl atoms react to destroy ozone according to the above reactions.
- Under conditions of Antarctic spring, not enough O• atoms are available to regenerate Cl atoms from ClO•.
- It is now known that ClO• forms the **ClO-OCl dimer**, which regenerates Cl• by the following reactions:
- $ClOOCl + h\nu \rightarrow ClOO\bullet + Cl\bullet$
- $ClOO\bullet + h\nu \rightarrow O2 + Cl\bullet$

Role of PSCs in the formation of the Antarctic O_3 hole

1. **PSCs promote the conversion of inorganic chlorine & chlorine reservoir species to active chlorine**

2. **PSC Enhance polar ClOx cycle**

1. PSCs promote the conversion of inorganic Cl and Cl reservoir species to active Cl

Pathway 1 : HCl(g) → Cl2 (g)

- **Absorption of gaseous HCl by PSCs occurs very efficiently**

  $HCl(g) \rightarrow HCl(s)$

- **Heterogeneous reaction of gaseous ClONO2 with HCl on the PSC particles**

  $HCl(s) + ClONO_2 \rightarrow HNO_3\ (s) + Cl_2$

  where s denotes the PSC surface

Note: The gas phase reaction between HCl and ClONO2 is extremely slow.

PSCs promote the conversion of inorganic Cl and Cl reservoir species to active Cl (Continued)

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- Pathway 2: $\mathrm{HCl(g)} \rightarrow \mathrm{ClNO2\ (g)}$ in the presence of $\mathrm{N2O5}$

  $\mathrm{HCl(g)} \rightarrow \mathrm{HCl(s)}$

  $\mathrm{HCl(s)} + \mathrm{N2O5} \rightarrow \mathrm{ClNO2} + \mathrm{HNO3\ (s)}$

- Pathway 3: $\mathrm{ClONO2(g)} \rightarrow \mathrm{HOCl\ (g)}$

  $\mathrm{ClONO2} + \mathrm{H2O\ (s)} \rightarrow \mathrm{HOCl} + \mathrm{HNO3\ (s)}$

The gas phase reactions between HCl and N2O5, between ClONO2 and H2O are too slow to be important.

Cont.,

The products, Cl_2, HOCl & $ClNO_2$, absorb light when spring comes to deplete O_3 as shown below:

- $Cl_2 + hv \longrightarrow 2Cl$
- $HOCl + hv \longrightarrow HO + Cl$
- $ClNO_2 + hv \longrightarrow Cl + NO_2$

- $O_3 + Cl \longrightarrow ClO + O_2$
- $\underline{ClO + O \longrightarrow Cl + O_2}$

Net: $O_3 + O \longrightarrow 2O_2$

Role 2 of PSC: Enhance polar ClOx cycle

- PSCs **retain gaseous nitrogen species through: formation of HNO3.3H2O** and formation of HNO3 from gaseous nitrogen species such as ClNO3 and N2O5.
- Chlorofluorocarbons (CFCs) are inert in the troposphere.
- CFCs undergo photochemical reactions in the stratosphere to release Cl radical through homolytic bond cleavage that degrade ozone
- $CF_2Cl_2 + hv \rightarrow CF_2Cl\bullet + Cl\bullet$
- The ClOx chain reaction: $O + O_3 \rightarrow 2O_2$

Polar ClOx cycle to remove O3

- The ClOx cycle requires atomic oxygen O i.e.
  - $ClO + O \rightarrow Cl + O_2$

- **Polar ClOx cycle**
  - $ClO + ClO + M \rightarrow ClO-ClO + M$
  - $ClO-ClO + h\nu \rightarrow ClOO + Cl$
  - $ClOO + h\nu \rightarrow Cl + O_2$

- **O_3 destruction**
  - $Cl + O_3 \rightarrow ClO + O_2$

How does the polar ClOx stop?

- The chain reaction is stopped when the ice particles melt, releasing adsorbed HNO_3
  - $HNO_3 + h\nu \rightarrow {\bullet}OH + NO_2$
- **NO_2 sequestrates ClO,** which shutdown the polar ClO_x chain reaction.
  - $NO_2 + ClO \rightarrow ClONO_2$
- **Role 3: Volcanoes can deplete O3.**
- This is not injection of chlorine into the stratosphere, but rather **the injection of sulfate aerosols** which change the radiation balance in the stratosphere by **scattering light, and which convert inactive chlorine compounds** to active, **O3 depleting form**.

Denitrification by PSCs enhances polar ClOx cycle

- PSCs removes gaseous N species (denitrification)
  - Major process: formation of nitric acid trihydrate (NAT) PSCs
  - Minor process: Formation of HNO3 from gaseous N species (e.g. ClONO2 and N2O5) and subsequent retention of HNO3(s).
  - As PSCs particles grow larger over the winter, they sink to lower altitudes, falling out of the stratosphere.

Denitrification by PSCs enhances polar ClOx cycle (Continued)

- If HNO_3 is <u>not</u> removed from the stratosphere, it releases NO_2 back to the stratosphere upon photolysis.

  $HNO_3 + h\nu \rightarrow OH + NO_2$

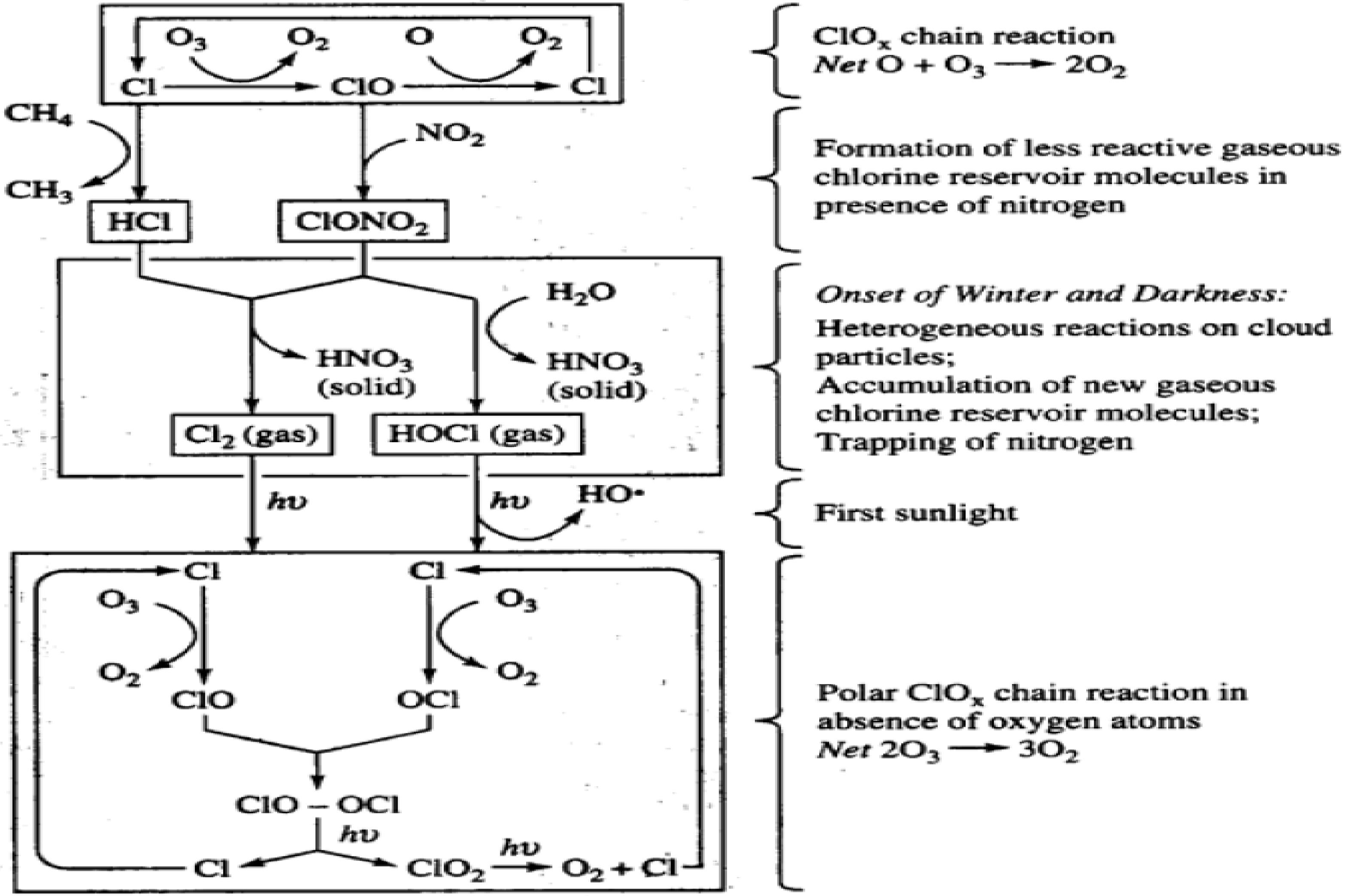
- The consequence of released NO_2 is to tie up active chlorine as $ClONO_2$ and make the ClOx polar cycle less efficient.

  $ClO + NO_2 \rightarrow ClONO_2$

Summary of the roles played by PSCs

- Provide surface for the conversion of inactive Cl species into active species
- Provide the media for removal of gaseous N species

Reaction sequence responsible for Antarctic ozone hole



ClO_x chain reaction
Net $O + O_3 \longrightarrow 2O_2$

Formation of less reactive gaseous chlorine reservoir molecules in presence of nitrogen

Onset of Winter and Darkness:
Heterogeneous reactions on cloud particles;
Accumulation of new gaseous chlorine reservoir molecules;
Trapping of nitrogen

First sunlight

Polar ClO_x chain reaction in absence of oxygen atoms
Net $2O_3 \longrightarrow 3O_2$

Summary: Ingredients for the Antarctica ozone hole formation

- Cold temperatures; cold enough for the formation of Polar Stratospheric Clouds.
  - Polar winter leading to the formation of the polar vortex which isolates the air within it.
  - As the vortex air is isolated, the cold temperatures persist.
  - This allows the growth of PSCs and subsequent sink to lower altitude, therefore removal of gaseous N species.
- Sunlight (to initiate O3 depletion reaction sequence).

Does ozone hole occur in the north pole (Arctic)?

- The Arctic winter stratosphere is generally warmer than the Antarctic by ~10k.
  - Caused by the water mass covering the Arctic.
- The warmer temperature results in less PSCs and shorter presence time.
- The less abundant and less persistent PSCs dramatically reduce the extent of denitrification.
  - PSCs in the Arctic does not have sufficient time to settle out of the stratosphere.
  - **PSCs releases their HNO3 back to the stratosphere, making ClOx polar cycle less efficient.**
- Conclusion: Ozone depletion is less dramatic in the Arctic compared with the Antarctic.

Summary on ozone hole

- Massive ozone loss requires both very cold temperature (to form PSCs) and sunlight (to photolyze reactive chlorine to produce Cl atoms).
- Denitrification is required to prevent reformation of reservoir species once photolysis ensures.
- Denitrification occurs when PSCs containing HNO3 settling out of the stratosphere.
- The massive springtime loss of ozone in the Antarctic stratosphere (the Ozone hole) is conclusively linked to anthropogenic halogens.
- Virtually all inorganic chlorine is converted into active chlorine every winter in both the Antarctic and Arctic stratosphere as a result of heterogeneous reactions of reservoir species on polar stratospheric clouds (PSCs).

Summary on ozone hole (Continued)

- The most important difference between the Antarctic and the Arctic stratosphere is the extent of denitrification that occurs.
- Because of generally warmer temperatures in the Arctic, PSCs tend not persist until the onset of sunlight, releasing their nitric acid back into the vapor phase.
- As a result, ozone depletion is generally less dramatic in the Arctic than the Antarctic.

Ozone depletion potential (ODP)

- ODP is used to facilitate comparison of harmfulness to the ozone layer by different chemicals.
- ODP of a compound is defined as the total steady-ozone destruction that results from per unit mass of species *i* emitted per year relative to that for a unit mass emission of CFC-11
- $$\mathrm{ODP}_i = \frac{\Delta O3_i}{\Delta O3CFC_{-11}}$$

ODPs of Selected Compounds

Compound	ODP
CFC-11 (CFCl3)	1.0
CFC-113 (CCl2FClF2)	0.8
CCl4	1.20
CFBr3	12
CH3CCl3	0.12
HCFC-22 (CF2HCl)	0.055
CH3Cl	0.02
CH3Br	0.64

3.5.3. Sources and reactions of HOx, ClOx and NOx in the stratosphere

❑ i) Sources & reactions of HOx in the stratosphere

- CH4 is stable in the troposphere, however,
- if it crosses the tropopause it under goes oxidation to give CO_2 and H_2O that subsequently undergoes photo-ionization to generate OH and H that degrades O_3 as shown below:
  - $CH_4 + O_2 + h\nu \rightarrow CO_2 + H_2O$
  - $H_2O + h\nu \rightarrow HO\bullet + H\bullet$
  - $O^* + H_2O \rightarrow 2HO\bullet$
  - $CH_4 + O \rightarrow CH_3\bullet + HO\bullet$
  - $H_2O_2 + h\nu \rightarrow 2\ HO\bullet$
  - $HNO_2 + h\nu \rightarrow NO + HO\bullet$

Reactions of •OH in the stratosphere

- $HO\bullet + O_3 \rightarrow HO_2\bullet + O_2$
- $\underline{HO_2\bullet + O_3 \rightarrow OH\bullet + 2O_2}$

Net reaction: $2O_3 \rightarrow 3O_2$

Hydroxyl and Hydroperoxyl Radicals in the Atmosphere

- hydroxyl radical, HO•, is the single most important reactive intermediate species in atmospheric chemical processes.
- It is formed by several mechanisms.
- At higher altitudes it is produced by photolysis of water:
  - $H_2O + h\nu \rightarrow HO\bullet + H$
  - $HONO + h\nu \rightarrow HO\bullet + NO$

Cont.,

- hydroxyl radical is produced as the result of the photolysis of ozone,
  - O3 + *h*v ($\lambda < 315$ nm) → O* + O2
- followed by the reaction of a fraction of the excited oxygen atoms with water molecules:
  - O* + H_2O → 2HO•

Cont.,

- Among the important atmospheric trace species carbon **monoxide, sulfur dioxide, hydrogen sulfide, methane**, and **nitric oxide**.
- **methane or carbon monoxide** react with hydroxyl radical most frequently removed from the troposphere by reaction with
  - $CH_4 + HO\bullet \rightarrow H_3C\bullet + H_2O$
  - $CO + HO\bullet \rightarrow CO_2 + H$

Cont.,

- The highly reactive methyl radical, $H_3C\bullet$, reacts with O_2,
  - $H_3C\bullet + O_2 \rightarrow H_3COO\bullet$ to form **methylperoxyl radical**, $H_3COO\bullet$.
- The hydrogen atom produced in the above reaction reacts with O_2 to produce **hydroperoxyl radical**:
  - $H + O_2 \rightarrow HOO\bullet$
- The hydroperoxyl radical can undergo **chain termination reactions, such as**
  - $HOO\bullet + HO\bullet \rightarrow H_2O + O_2$
  - $HOO\bullet + HOO\bullet \rightarrow H_2O_2 + O_2$
- or reactions that **regenerate** hydroxyl radical:
  - $HOO\bullet + NO \rightarrow NO_2 + HO\bullet$
  - $HOO\bullet + O_3 \rightarrow 2O_2 + HO\bullet$

HO• Concentration abundances

- Because of the higher humidity and higher incident sunlight which result in elevated O* levels, the **concentration of HO• is higher in tropical regions.**
- The southern hemisphere probably has about a 20% higher level of HO• than does the northern hemisphere because of greater production of anthropogenic,
- **HO•-consuming CO in the northern hemisphere**.
- The hydroperoxyl radical, HOO•, is an intermediate in some important chemical reactions.

iii) Sources & reactions of ClOx in thestratosphere

- Chlorofluorocarbons (CFCs) are inert in the troposphere.
- CFCs undergo photochemical reactions in the stratosphere to release Cl radical through homolytic bond cleavage that degrade ozone
  - $CF2Cl2 + hv \rightarrow CF2Cl\bullet + Cl\bullet$
  - $Cl\bullet + O3 \rightarrow ClO + O2$
  - $\underline{ClO + O \rightarrow Cl + O2}$
- **Net reaction: $O3 + O \rightarrow 2O2$**

Cont.,

- Termination reactions:
  - $\mathrm{Cl + CH4 \rightarrow HCl + CH3}$
  - $\mathrm{ClO + NO2 + M \rightarrow ClNO3 + M}$
- HCl & ClNO3 are reservoirs of Cl. Therefore, how does Cl released from its reservoirs?
  - $\mathrm{ClNO3 + hv \rightarrow Cl + NO3}$
  - $\mathrm{HCl + OH \rightarrow Cl + H2O}$

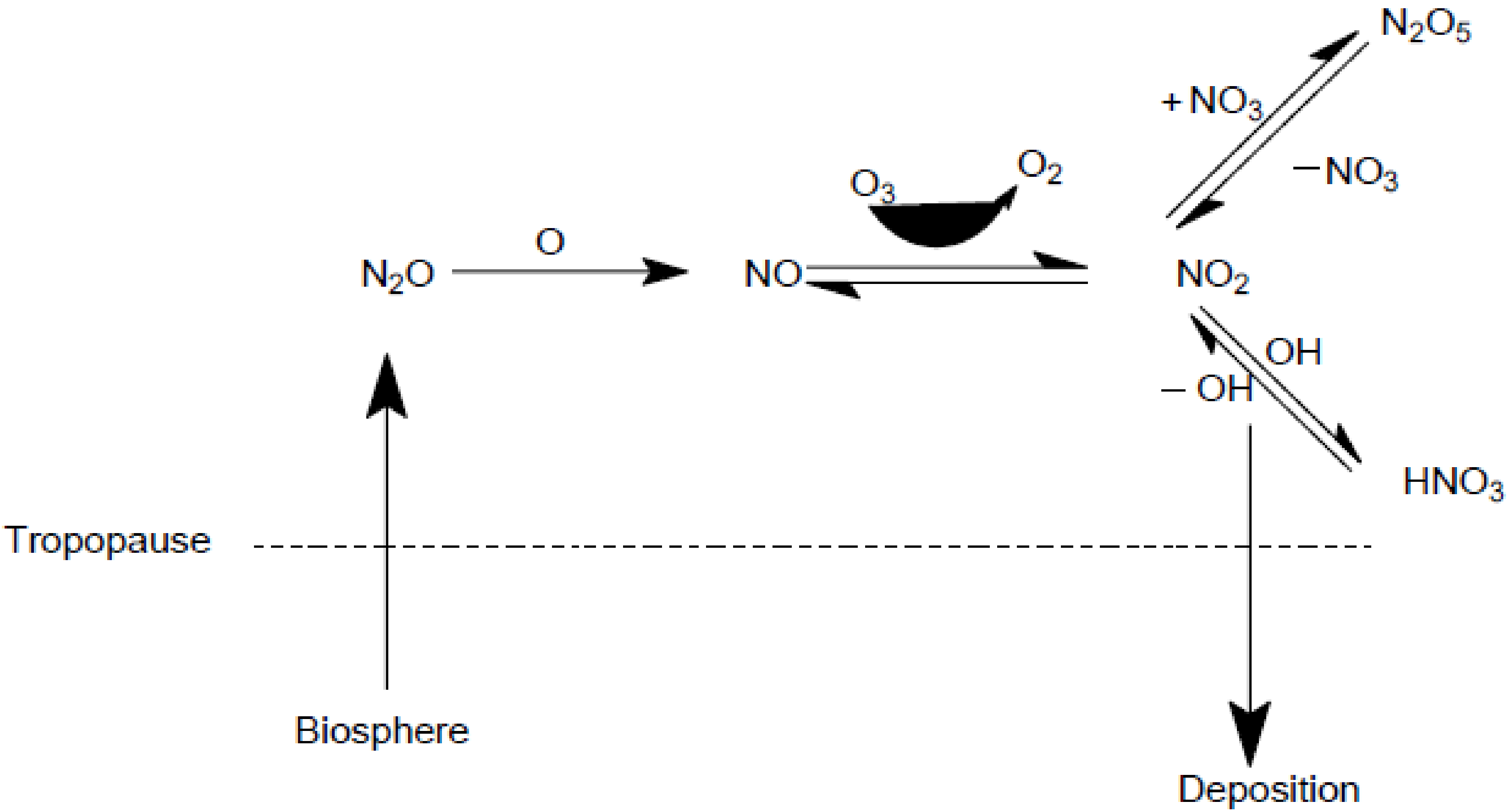
iv) Sources & reactions of NOx in the stratosphere

- Biospheric N_2O from nitrification and denitrification is stable in the troposphere and cross the tropopause without change:
  - $O + N_2O \rightarrow 2NO$ (5 %) &
  - $N_2O + h\nu \rightarrow N_2 + O$ (95 %)
- **NOx cycle**
  - $NO + O_3 \rightarrow NO_2 + O_2$
  - $\underline{NO_2 + h\upsilon \rightarrow NO + O}$
- **Net rxn :** $\boldsymbol{O_3 + h\upsilon \rightarrow O_2 + O}$
  - $O + NO_2 \rightarrow NO + O_2$
  - $\underline{NO \overset{M}{+} O_3 \rightarrow NO_2 + O_2}$
- **Net rxn:** $\boldsymbol{O + O_3 \rightarrow 2O_2 + M}$

Cont.,

- **Termination reactions**
- **Daytime :** $NO_2 + OH\bullet + M \rightarrow HNO_3 + M$
- **Night time :** $NO_2 + O_3 \rightarrow NO_3 + O_2$
  - $NO_3 + NO_2 \rightarrow N_2O_5 + M$
- HNO_3 and N_2O_5 have a longer lifetime than NOx. Thus they are reservoirs of NOx
- **Conversion from the reservoirs**
  - $HNO_3 + hv \rightarrow NO_2 + OH\bullet$
  - $HNO_3 + OH\bullet \rightarrow NO_3 + H_2O$
  - $NO_3 + hv \rightarrow NO_2 + O$
  - $N_2O_5 + hv \rightarrow NO_3 + NO_2$

Reactions of NOx



v) Reactions of atmospheric oxygen

- Oxygen in the troposphere plays a strong role in processes that occur on the earth‘s surface. Atmospheric oxygen takes part in energy-producing reactions, such as the burning of fossil fuels:
- **$\mathrm{CH4}$ (in natural gas**
- oxidative weathering processes consume oxygen, such as:
- **$\mathrm{4FeO + O2 \rightarrow 2Fe2O3}$. s) + $\mathrm{2O2 \rightarrow CO2 + 2H2O}$**
- Oxygen is returned to the atmosphere through plant photosynthesis:
- **$\mathrm{CO2 + H2O} + h\nu \rightarrow \{\mathrm{CH2O}\} + \mathrm{O2}$**

Cont.,

- Because of the extremely rarefied atmosphere and the effects of ionizing radiation, elemental oxygen in the upper atmosphere exists to a large extent in forms other than diatomic O_2.
- In addition to O_2, the upper atmosphere contains oxygen atoms, O; excited oxygen molecules, O_2^*; and ozone, O_3.
- Atomic oxygen is produced by a photochemical reaction: **$O_2 + hv \rightarrow O + O$**
- Oxygen atoms in the atmosphere can exist in the ground state (O) and in excited states (O^*). These are produced by the photolysis of ozone
- $O_3 + hv(\lambda < 308\ \text{nm}) \rightarrow O^* + O_2$

Cont.,

- **The overall reaction: $2O3 \rightarrow 3O2$,** is favored thermodynamically so that ozone is inherently unstable.
- Its decomposition in the stratosphere is catalyzed by a number of natural and pollutant trace constituents, including NO, NO2, H, HO•, HOO•, ClO, Cl, Br, and BrO.
- Ozone decomposition also occurs on solid surfaces, such as metal oxides and salts produced by rocket exhausts.

vi) Reactions of atmospheric Nitrogen

- The 78% by volume of nitrogen contained in the atmosphere constitutes an inexhaustible reservoir of that essential element.
- A small amount of nitrogen is fixed in the atmosphere by lightning, and some is also fixed by combustion processes, particularly in internal combustion and turbine engines.
- Before the use of synthetic fertilizers reached its current high levels, chemists were concerned that denitrification processes in the soil would lead to nitrogen depletion on the Earth.
- Now, with millions of tons of synthetically fixed nitrogen being added to the soil each year, major concern has shifted to possible excess accumulation of nitrogen in soil, fresh water, and the oceans.

Cont.,

- Unlike oxygen, which is almost completely dissociated to the monatomic form in higher regions of the thermosphere, molecular **nitrogen is not readily dissociated by ultraviolet radiation.**
- However, at altitudes exceeding approximately 100 km, atomic nitrogen is produced by photochemical reactions: $N_2 + h\nu \rightarrow N + N$
- Other reactions which may produce monatomic nitrogen are:
- $N_2^+ + O \rightarrow NO^+ + N$
- $NO^+ + e^- \rightarrow N + O$
- $O^+ + N_2 \rightarrow NO^+ + N$

Cont.,

- **An ion formed from NO, the NO^+ ion, is one of the predominant ionic species in the so-called E region of the ionosphere.**
- Pollutant oxides of nitrogen, particularly NO_2, are key species involved in air pollution and the formation of photochemical smog.
- For example, NO_2 is readily dissociated photochemically to NO and reactive atomic oxygen:
  - $NO_2 + h\nu \rightarrow NO + O.$
- **This reaction is the most important primary photochemical process involved in smog formation.**

vii) Effect of Atmospheric carbon dioxide

- Although only about 0.035% (350 ppm) of air consists of carbon dioxide, it is the atmospheric non pollutant species of most concern.
- Carbon dioxide, along with water vapor, is primarily responsible for the absorption of infrared energy re-emitted by the earth such that some of this energy is reradiated back to the earth‘s surface.
- Current evidence suggests that changes in the atmospheric carbon dioxide level will substantially alter the earth‘s climate through the greenhouse effect.

Cont.,

- The most obvious factor contributing to increased atmospheric carbon dioxide is consumption of carbon-containing fossil fuels.
- In addition, release of CO_2 from the biodegradation of biomass and uptake by photosynthesis are important factors determining overall CO_2 levels in the atmosphere.
- Therefore, the current worldwide destruction of forests and conversion of forest lands to agricultural uses contributes substantially to a greater overall increase in atmospheric CO_2 levels.

viii) Effect of Atmospheric water

- The water vapor content of the troposphere is normally within a range of 1–3% by volume with a global average of about 1%.
- However, air can contain as little as 0.1% or as much as 5% water.
- The percentage of water in the atmosphere decreases rapidly with increasing altitude.
- Water vapor absorbs infrared radiation even more strongly than does carbon dioxide, thus greatly influencing the earth‘s heat balance.
- Clouds formed from water vapor reflect light from the sun and have a temperature-lowering effect.

Cont.,

- On the other hand, water vapor in the atmosphere acts as a kind of blanket at night, retaining heat from the earth‘s surface by absorption of infrared radiation.
- Thus, little water is transferred from the troposphere to the stratosphere, and the main source of water in the stratosphere is the photochemical oxidation of methane:
    - $\mathbf{CH4 + 2O2 + \mathit{h}v}$ **(several steps)** $\mathbf{\rightarrow CO2 + 2H2O}$.
- The water thus produced serves as a source of stratospheric hydroxyl radical as shown by the following reaction:
    - $\mathbf{H2O + \mathit{h}v \rightarrow HO\bullet + H}$

3.5.4 Reactions in Thermosphere

❑***Let warm up yourself with the following activities***

a) What is Thermosphere?
b) Mention some of the dominant species in the Thermosphere
c) Explain the source and effects of species in the Thermosphere
d) Describe the common reactions in the Thermosphere

Cont.,

- Thermosphere is one of the stratification of atmosphere.
- It is rich in Oxygen atom; hence two types of reactions are common in Thermosphere; these are:
  - i) photo-dissociation
  - ii) photo-ionization

i) Photo-dissociation

- This reaction involves the rapture of chemical bonds from the absorption of photons to form atoms or molecules:
- **$O_2 + h\nu \rightarrow 2O + 120$ kcal/mol**
- This reaction absorbs most of the high energy radiation.
- It releases considerable amount of heat that is responsible for the increase in temperature in the thermosphere.
- In this region 99% of the available oxygen is in the form of atomic oxygen and the dissociation of nitrogen is limited because of stable triple bonds in molecular nitrogen

ii) Photo-ionization

- This reaction generates ions by absorption of photons and ejection of single electrons from molecules.
- N_2, O_2, & O absorb radiations of $\lambda < 240$ nm.
  - $O_2 + h\nu \rightarrow O_2^+ + e^-$
  - $O + h\nu \rightarrow O^+ + e^-$

3.6 Atmospheric Pollution

- Do you know some of the causes for Atmospheric Pollution

✓Let warm up yourself with this questions

a) What is Atmospheric Pollution

b) Mention the common atmospheric pollutants

c) Describe the source of atmospheric pollutants

d) Explain the nature and classification of atmospheric pollutants

Air pollution

- Presence in the outdoor or indoor atmosphere of one or more *contaminants* (Chemical, Physical, biological) in quantities and duration that can injure human, plant or animal life or material properties or which unreasonable interferes with the enjoyment of life or the conduct of business

Atmospheric Pollution

- Atmospheric (air) pollution occurs when the **concentration of certain substances become high enough to toxify the atmospheric** environment.
- Common air pollutants such as:
- oxides of sulfur (**SOx)**, oxides of nitrogen (**NOx)**, oxides of **carbon(CO & CO_2**), **CH_4, C_6H_6**, Ground level **O_3,** Volatile organic compounds (**VOC**), Chlorofluorocarbon(CFC) and heavy metals such as (Pb).

3.6.1.Nature and classification of atmospheric pollutants

☐The main atmospheric pollutants are

- particles in the atmosphere,
- gaseous inorganic pollutants, gaseous organic pollutants,
- photochemical smog, green house and global warming,
- nuclear winter and
- acid rain.

Air pollution: units

- $g.m^{-3}$ vs. ppm_v (parts per million)
- 1 ppm_v = 1 molecule per million (10^6)molecules
  = 1.10^{-6} m^3/m^3 = 1 ml/m^3
- 1 ppb_v = 1 molecule per billion (10^9) molecules
  = 1.10^{-9} m^3/m^3 = 1 $\mu l/m^3$

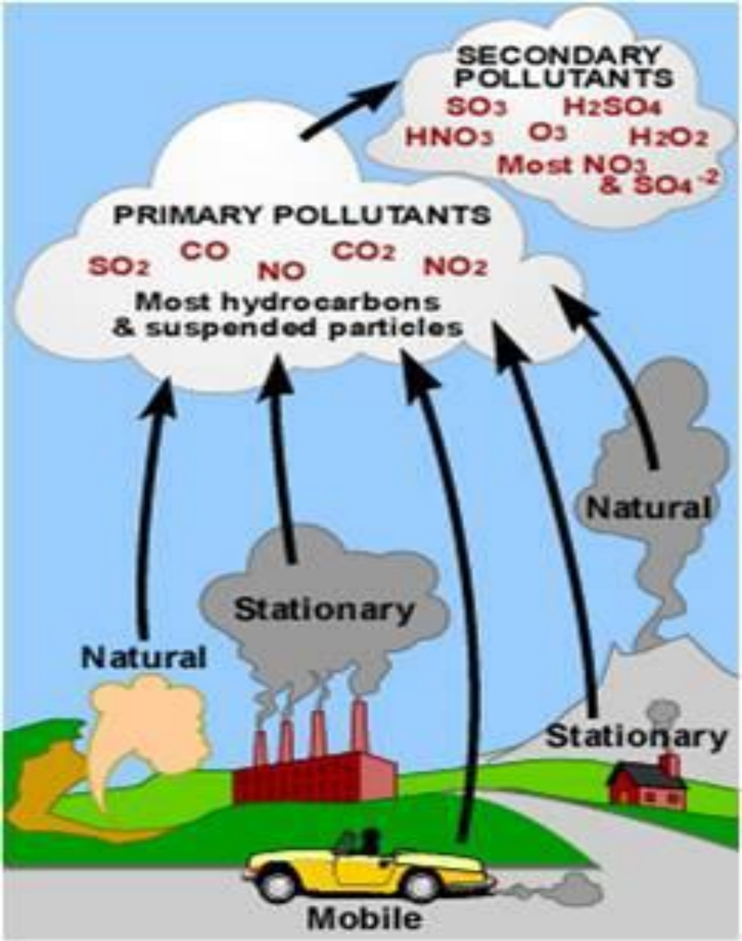
Types of Pollutants

❑ **Primary:**

pollutants that exist in the same form as in source emissions

❑ **Secondary:**

pollutants which result from transformations of primary pollutants (hydrolysis, oxidation, photochemical oxidation) into other chemical species



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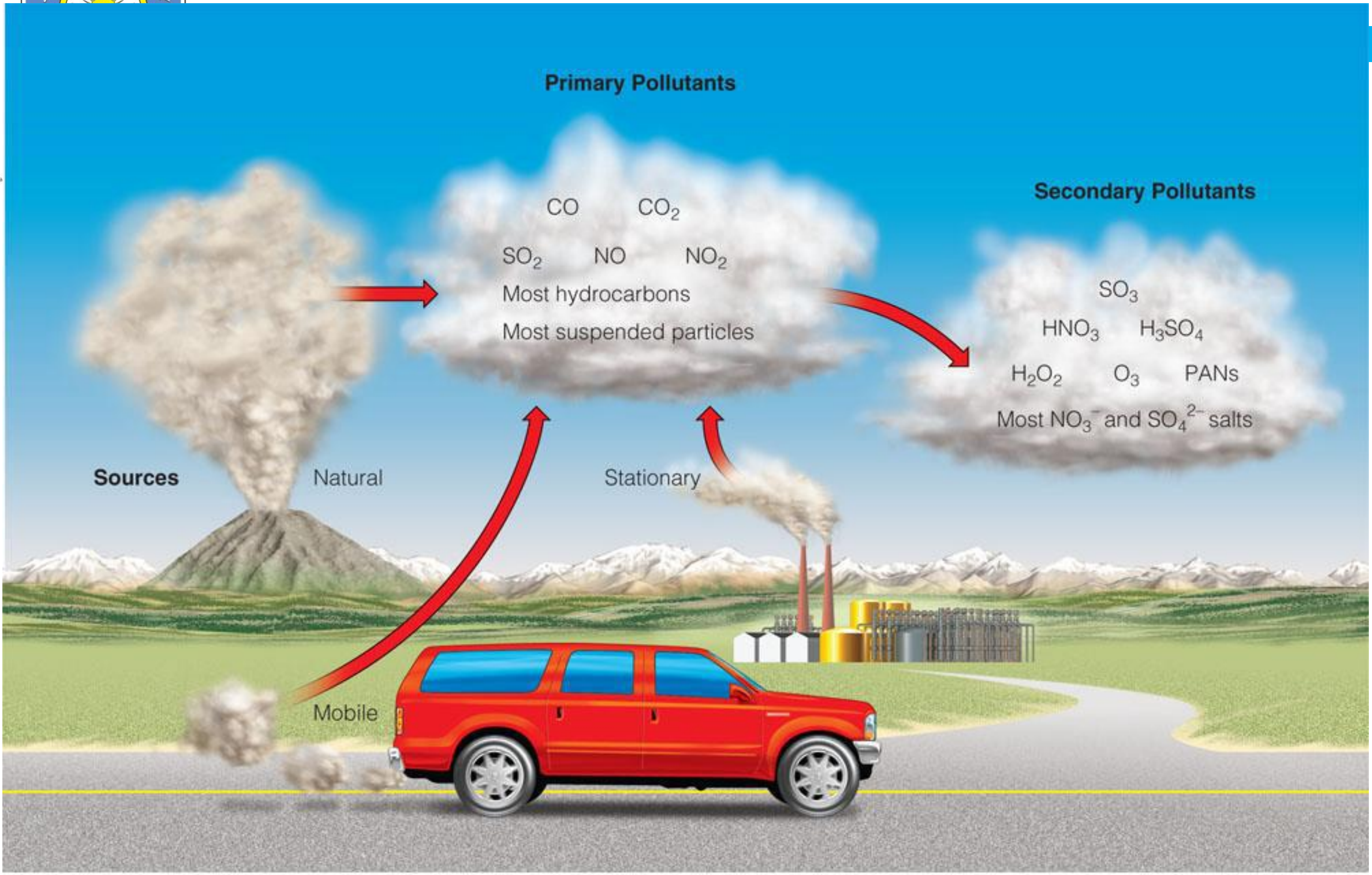

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Sources of pollutants

- **Natural Sources** – Biogenic and geogenic emissions from wildfires, wind blown dust, plants, trees, grasses, volcanoes, geysers, seeps, soil, and lightning

Anthropogenic sources

Point Sources – Generally a major facility emitting pollutants from identifiable sources (pipe or smoke stack).

Cont.,

- **Area source** – Any low-level source of air pollution released over a diffuse area (not a point) such as consumer products, architectural coatings, waste treatment facilities, animal feeding operations, construction, open burning, residential wood burning, swimming pools, and char broilers

Cont.,

- **Mobile Sources**
- On-road includes any moving source of air pollution such as cars, trucks, motorcycles, and buses
- Non-road sources include pollutants emitted by combustion engines on farm and construction equipment, locomotives, commercial marine vessels, recreational watercraft, airplanes, snow mobiles, agricultural equipment, and lawn and garden equipment

3.6.2 Particles in the atmosphere as means of air pollution

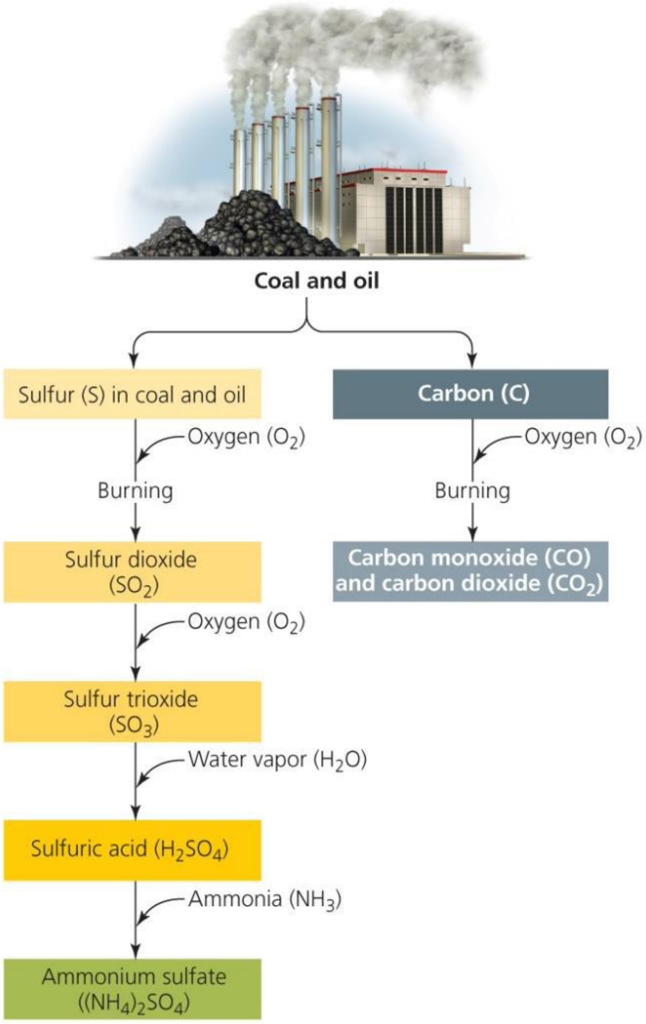
a) What are particles?

b) Explain the physical and chemical processes for particle formation

c) Mention the effects of particles on the atmosphere

d) Explain how Control of particulate emissions can be controlled

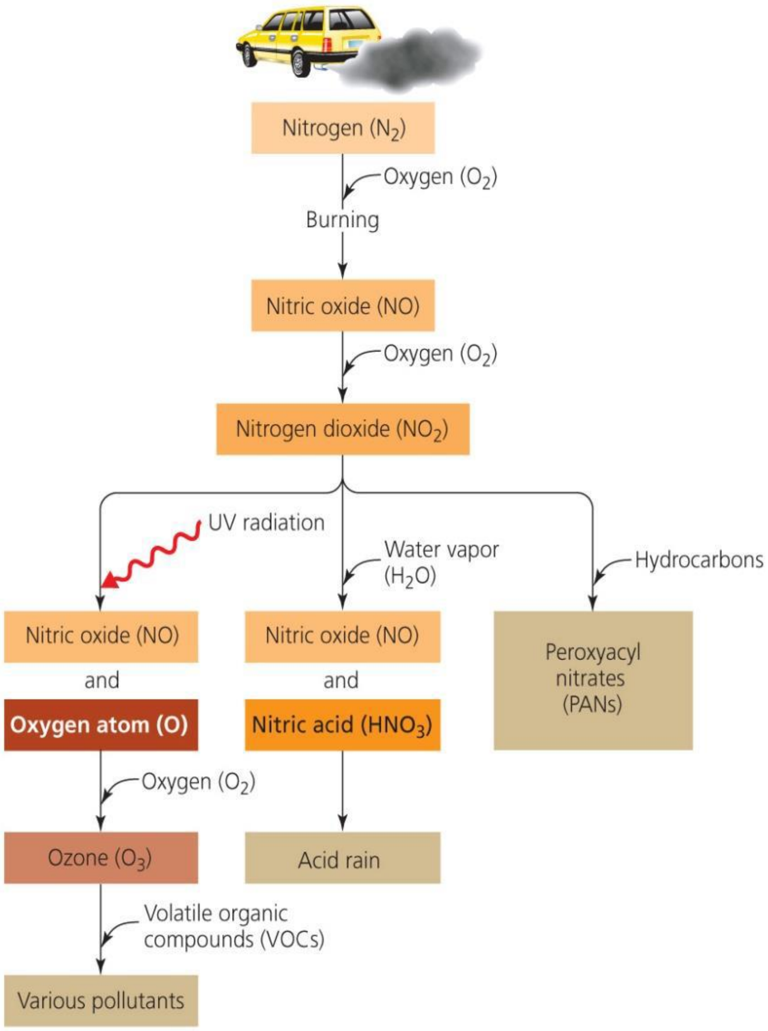
Industrial smog Photochemical smog


Coal and oil

Sulfur (S) in coal and oil
Oxygen (O_2)
Burning
Sulfur dioxide (SO_2)
Oxygen (O_2)
Sulfur trioxide (SO_3)
Water vapor (H_2O)
Sulfuric acid (H_2SO_4)
Ammonia (NH_3)
Ammonium sulfate ($(NH_4)_2SO_4$)

Carbon (C)
Oxygen (O_2)
Burning
Carbon monoxide (CO) and carbon dioxide (CO_2)

(a) Burning sulfur-rich oil or coal without adequate pollution control technologies


Nitrogen (N_2)
Oxygen (O_2)
Burning
Nitric oxide (NO)
Oxygen (O_2)
Nitrogen dioxide (NO_2)

UV radiation
Nitric oxide (NO) and Oxygen atom (O)
Oxygen (O_2)
Ozone (O_3)
Volatile organic compounds (VOCs)
Various pollutants

Water vapor (H_2O)
Nitric oxide (NO) and Nitric acid (HNO_3)
Acid rain

Hydrocarbons
Peroxyacyl nitrates (PANs)

(a) Formation of photochemical smog

Definitions

- Particles in the atmosphere, which **range in size from about one-half millimeter down to molecular dimensions**, are made up of an amazing variety of materials and discrete objects that may consist of **either solids or liquid droplets**.
- are a term that has come to stand for particles in the atmosphere, although ***particulate matter*** **or simply** ***particles,*** is preferred usage.
- Particulate matter such as **PM10, PM2.5, PM1 and PM0.1** is defined as the fraction of particles with an aerodynamic diameter smaller than 10, 2.5, 1 and 0.1 respectively.

PMx = particulate matter with aerodynamic diameter < x μm

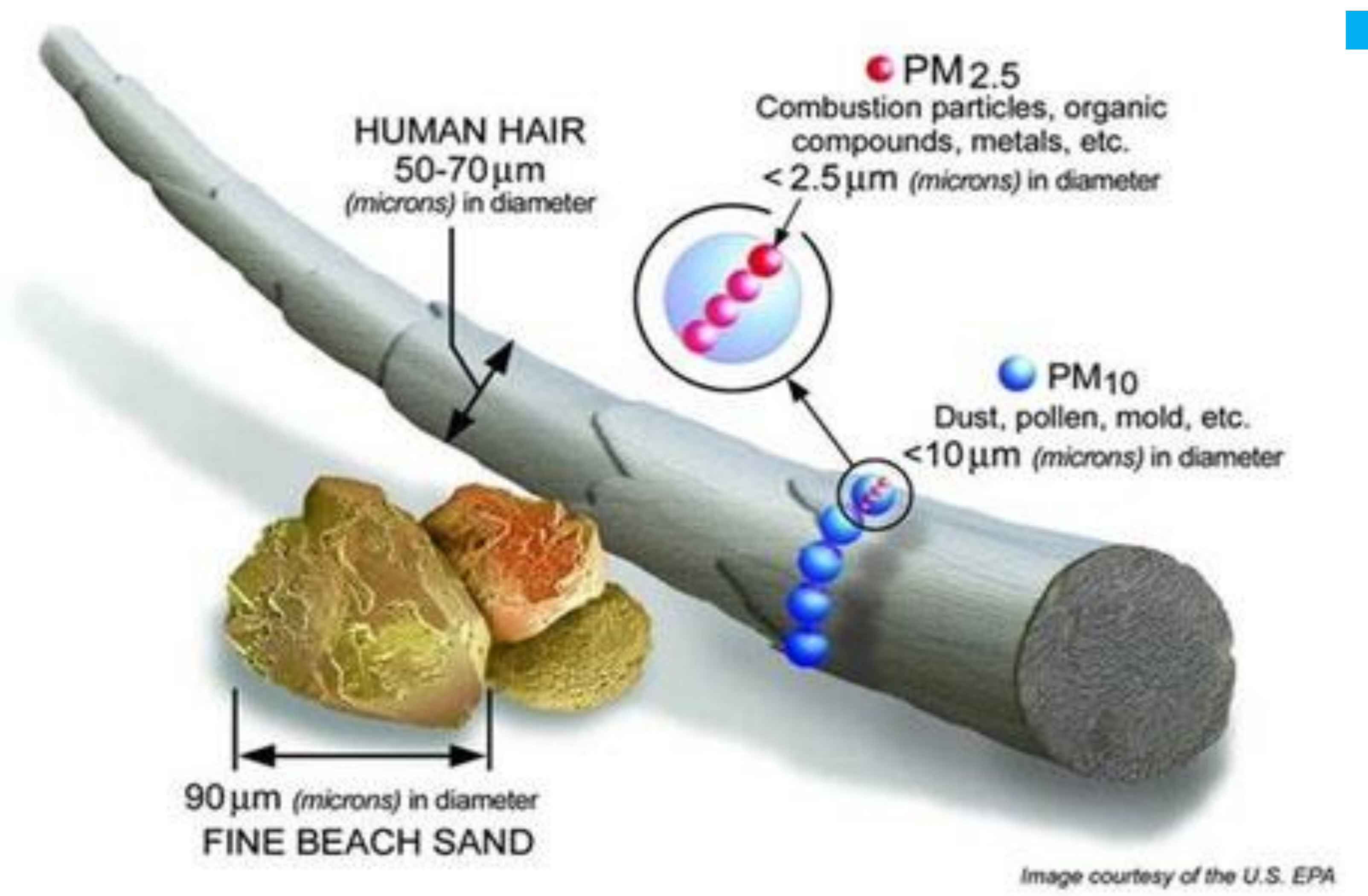


Image courtesy of the U.S. EPA

Cont.,

- **PM**$_{10}$ is particulate matter **10** micrometers or less in diameter,
- **PM**$_{2.5}$ is particulate matter 2.5 micrometers or less in diameter. **PM**$_{2.5}$ is generally described as fine particles.
- For comparison, a **human hair is about 100 micrometres,**
- EPA has developed ambient air quality trends for particle pollution, also called Particulate Matter (**PM**). **PM**$_{10}$ describes inhalable particles, with diameters that are generally **10** micrometers and smaller.

Important terms describing atmospheric particles

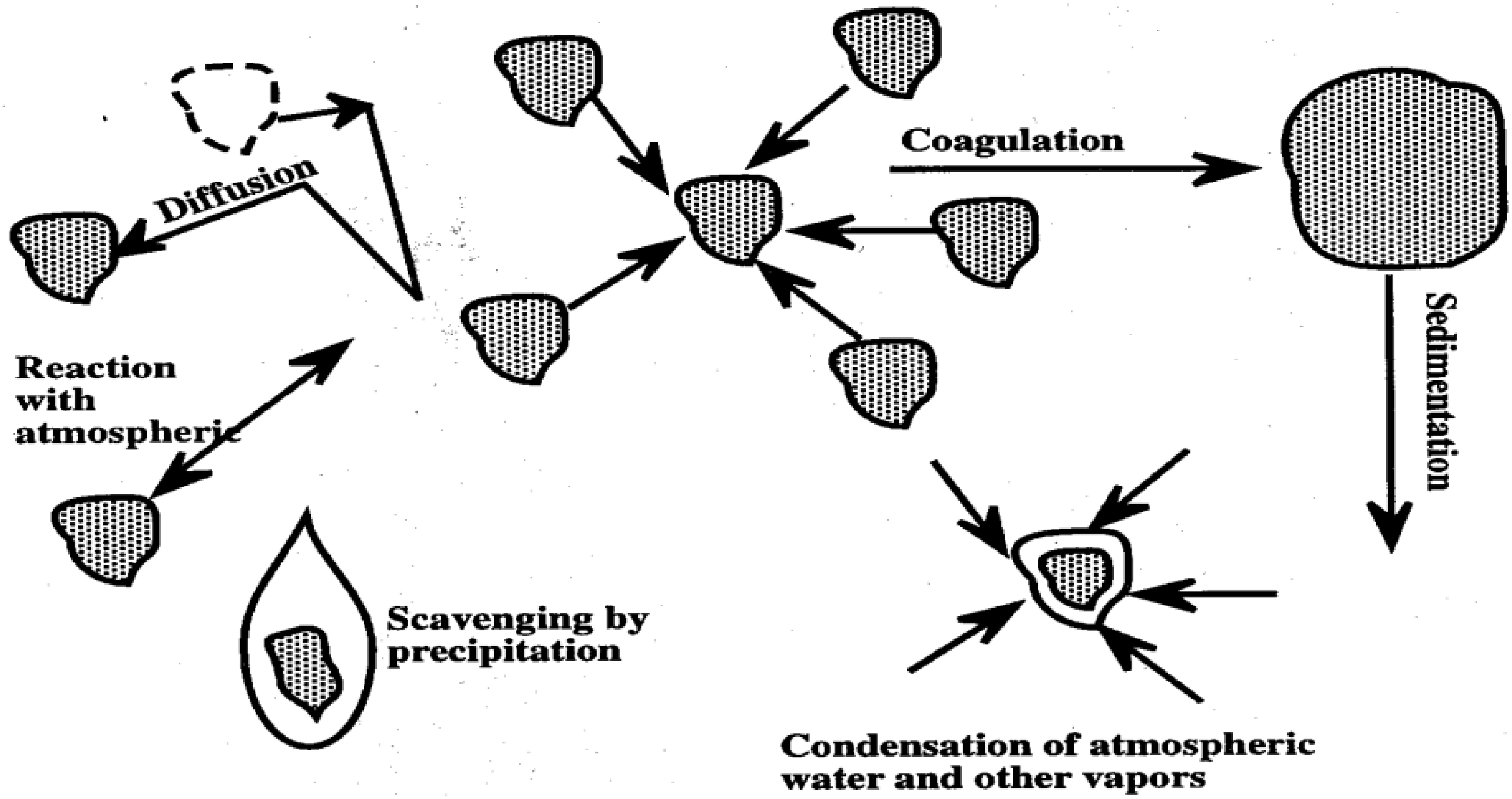
- **Aerosols:** Colloidal sized atmospheric particles
- Condensation aerosols: Formed by condensation of vapors or reactions of gases
- Atmospheric **aerosols** are solid or liquid particles smaller than 100 µm in diameter.
- **Dispersion:** aerosols Formed by grinding of solids, atomization of liquids, or dispersion of dusts
- **Fog:** Term denoting high level of water droplets
- **Haze:** Denotes decreased visibility due to the presence of particles
- **Mists:** Liquid particles
- **Smoke:** Particles formed by incomplete combustion of fuel

Smog=fog + smoke

3.6.2.1 Physical behavior of particles in the atmosphere

- atmospheric particles undergo a number of processes in the atmosphere.
- Small colloidal particles are subject to ***diffusion processes.***
- Smaller particles ***coagulate*** **together** to form larger particles.
- ***Sedimentation or dry deposition*** of particles, which have often reached sufficient size to settle by coagulation, is one of two major **mechanisms for particle removal from the atmosphere**.
- The other is ***scavenging*** **by raindrops** and other forms of precipitation.
- Particles **also react** with atmospheric gases.

Figure 3.6.1 Processes that particle undergo in the atmosphere.



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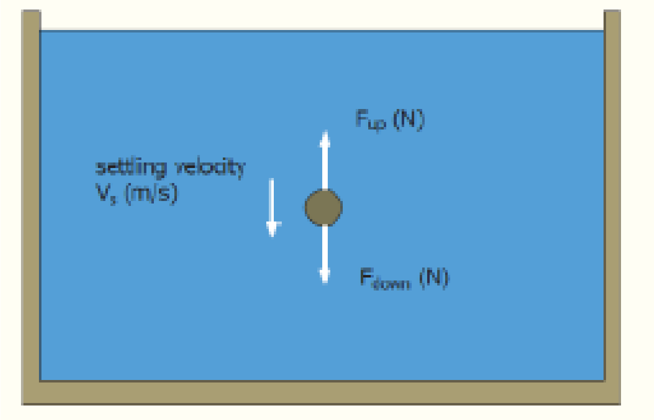
- **Particle size** usually expresses the **diameter of a particle,** though sometimes it is used to denote the radius.
- The rate at which a particle settles is a function of **particle diameter and density**.
- The settling rate is important in determining the effect of the particle in the atmosphere. For spherical particles greater than approximately 1 μm in diameter, Stokes‘ law applies,
  - $V = gd2(\rho1 – \rho2)/ 18\eta$

Cont.,

- Settling of solid particles under the influence of gravity, in a liquid of lower density



- Settling velocity ~ density & (particle diameter)^2
- The larger and heavier the particles, the better the settling

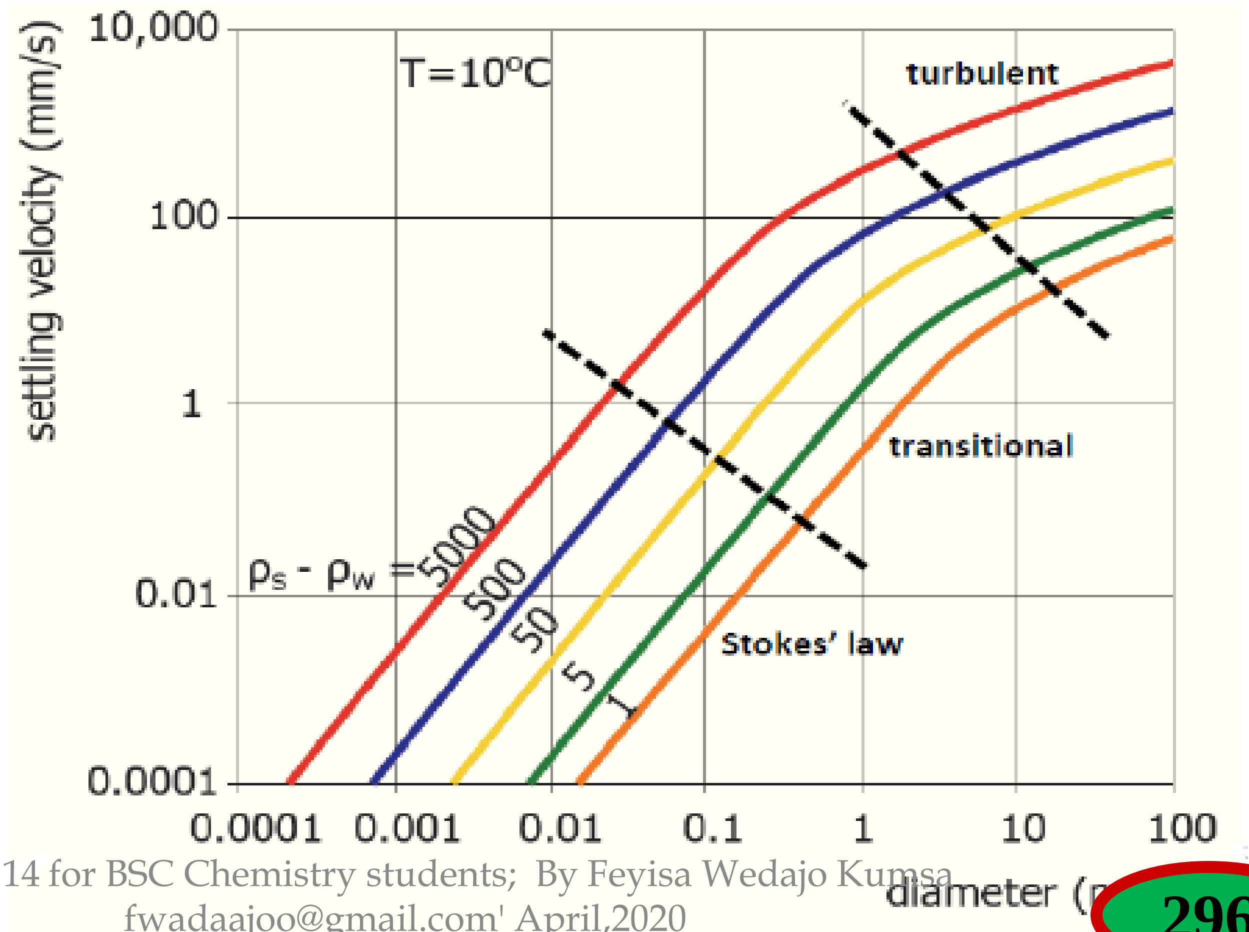
Cont.,

- where V is the settling velocity in cm/sec, g is the acceleration of gravity in cm/sec2, ρ1 is the density of the particle in g/cm3, ρ2 is the density of air in g/cm3, and η is the viscosity of air in poise.
- Stokes‘ law can also be used to express the effective diameter of an irregular nonspherical particle. These are called **Stokes diameters** (aerodynamic diameters) and are normally the ones given when particle diameters are expressed.
- Furthermore, since the density of a particle is often not known, an arbitrary density of 1 g/cm3 is conventionally assigned to ρ1; when this is done, the diameter calculated from Equation is called the **reduced sedimentation diameter**.

Cont.,

- In most practical cases:

  $d_p < 0.01 - 1mm$ laminar settling



Size and Settling of Atmospheric Particles

- Most kinds of aerosol particles have unknown diameters and densities and occur over a range of sizes. For such particles, the term **mass median diameter (MMD) may be used to describe aerodynamically equivalent spheres** having an assigned density of 1 g/cm3 at a 50% mass collection efficiency, as determined in sampling devices calibrated with spherical aerosol particles having a known, uniform size.
- (Polystyrene latex is commonly used as a material for the preparation of such standard aerosols.) The determination of MMD is accomplished by **plotting the log of particle size as a function of the percentage of particles smaller than the given size** on a probability scale.

Cont..

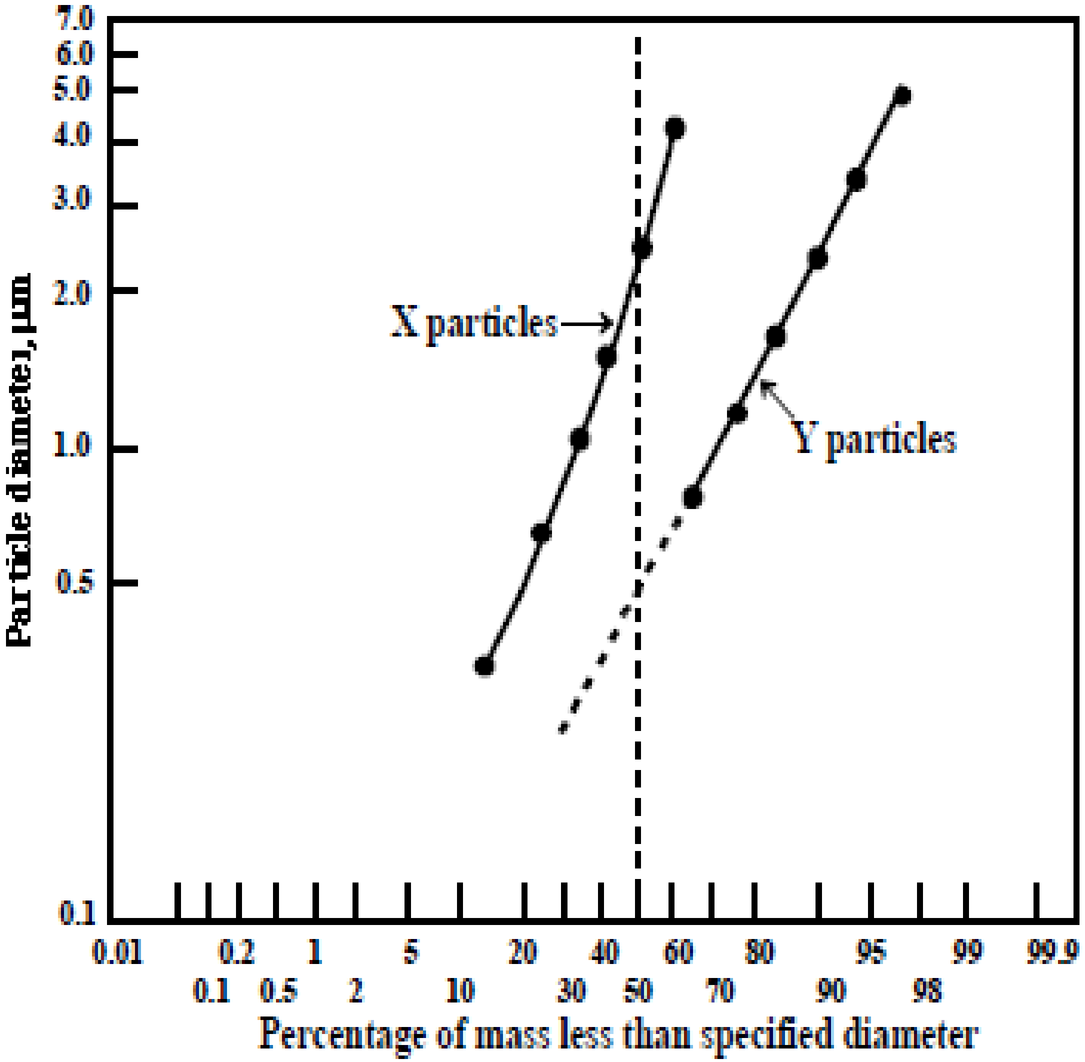


Fig 3. **Particle size distribution for particles of X (MMD = 2.0 µm) and Y (MMD = 0.5 µm).**

It is seen from the plot that particles of aerosol X have a mass median diameter of 2.0 µm (ordinate corresponding to 50% on the abscissa). In the case of aerosol Y, linear extrapolation to sizes below the lower measurable size limit of about 0.7 µm gives an estimated value of 0.5 µm for the MMD.

Case of Settling deviate from Stokes'

1. The settling characteristics of particles smaller than **about 1 μm in** diameter deviate from Stokes' Law because the settling particles "slip between" air molecules.

- Extremely small particles are subject to **Brownian motion** resulting from random movement due to collisions with air molecules and do not obey Stokes' Law.

2. Deviations are also observed for particles above **10 μm in** diameter because **they settle rapidly and generate turbulence as they fall.**

3.6.1.3. Physical processes for particle formation

- **Dispersion aerosols**, such as dusts, formed from the disintegration of larger particles are usually above 1 μm in size.
- Typical processes for forming dispersion aerosols include evolution of **dust from coal grinding, formation of spray in cooling towers, and blowing of dirt from dry soil.**
- Many dispersion aerosols originate from natural sources such as **sea spray, windblown dust, and volcanic dust.**
- However, vast varieties of human activities break up material and disperse it to the atmosphere.
- Most dispersion aerosols are relatively large. Larger particles tend to have fewer harmful effects than smaller ones.
- As examples, larger particles are less *respirable* in that they do not penetrate so far into the lungs as smaller ones, and larger particles are relatively easier to remove from air pollution effluent sources.

3.6.1.4. Chemical processes for particle formation

- Chemical processes in the atmosphere convert large quantities of atmospheric gases to particulate matter.
- Among the chemical species most responsible for this conversion are the **organic pollutants and nitrogen oxides that cause formation of ozone** and photochemical smog in the troposphere.
- To an extent, therefore, control of hydrocarbon and NOx emissions to reduce smog will also curtail atmospheric particulate matter pollution.
- A major fraction of ambient particulate matter arises from atmospheric gas-to particle conversion. Attempts to reduce particulate matter levels **require control of the same organic and nitrogen oxide (NOx) emissions that are precursors to urban** and regional ozone formation.

Cont.,

- Most chemical processes that produce particles are combustion processes, including **fossil-fuel-fired power plants; incinerators; home furnaces, fireplaces, and stoves; cement kilns; internal combustion engines; forest, brush, and grass fires; and active volcanoes.**

3.6.1.5 Inorganic Particles

- Metal oxides constitute a major class of inorganic particles in the atmosphere.
- These are formed whenever fuels containing metals are burned.
- For example, particulate iron oxide is formed during the combustion of pyrite-containing coal: $\mathbf{3FeS2 + 8O2 \rightarrow Fe3O4 + 6SO2}$
- Part of the calcium carbonate in the ash fraction of coal is converted to calcium oxide and is emitted into the atmosphere through the stack:

$$\mathbf{CaCO3 + heat \rightarrow CaO + CO2}$$

Cont.,

- A common process for the formation of aerosol mists involves the oxidation of atmospheric sulfur dioxide to sulfuric acid, a hygroscopic substance that accumulates atmospheric water to form small liquid droplets: $\mathbf{2SO_2 + O_2 + 2H_2O \rightarrow 2H_2SO_4}$
- In the presence of basic air pollutants, such as ammonia or calcium oxide, the sulfuric acid reacts to form salts:

$$\mathbf{H_2SO_4(droplet) + 2NH_3(\mathit{g}) \rightarrow (NH_4)_2SO_4\ (droplet)}$$

$$\mathbf{H_2SO_4(droplet) + CaO(\mathit{s}) \rightarrow CaSO_4(\ droplet) + H_2O}$$

Under low-humidity conditions water is lost from these droplets and a solid aerosol is formed.

i) The composition of Inorganic particles

$$2SO_2 + O_2 + 2H_2O \rightarrow 2H_2SO_4$$

$$H_2SO_4 + 2NaCl(\text{particulate}) \rightarrow Na_2SO_4(\text{particulat}$$

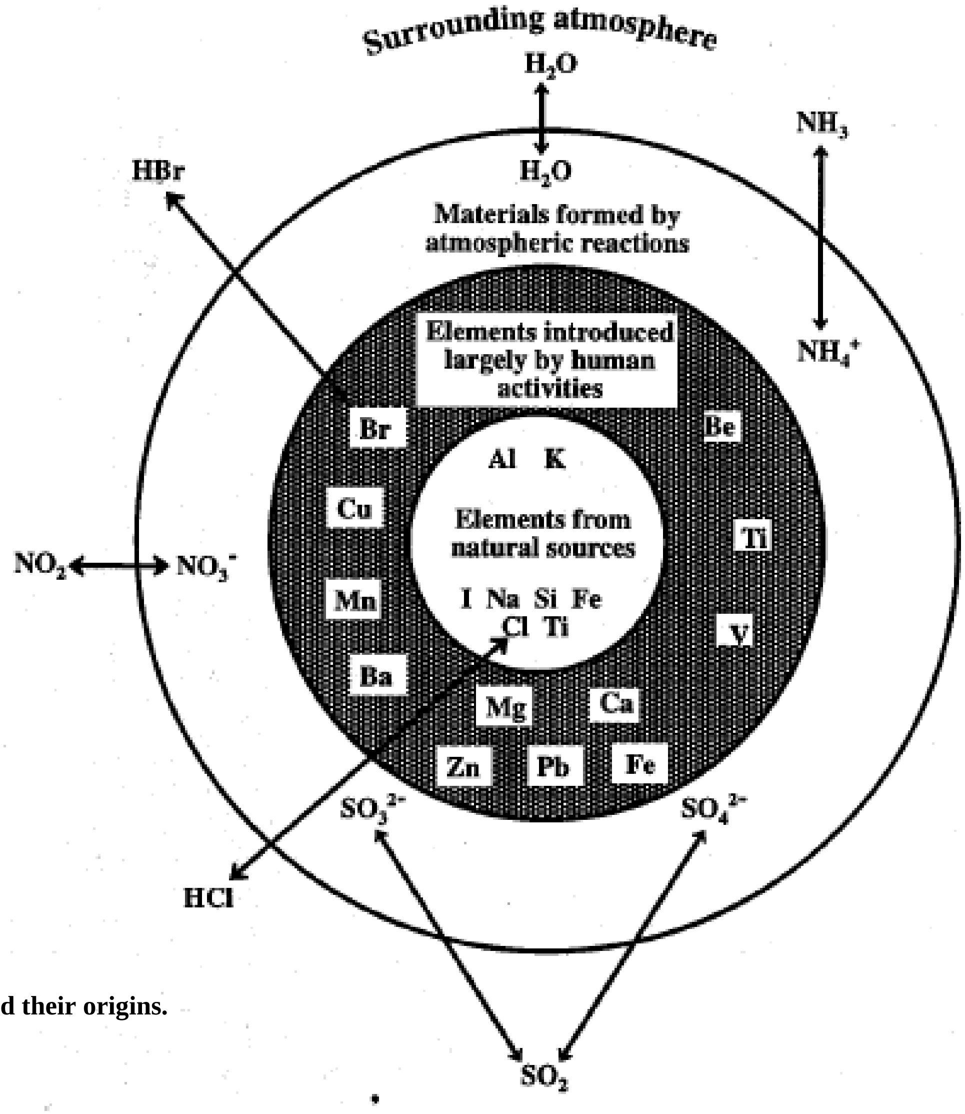


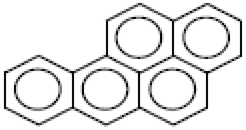
Figure 3.4. Some of the components of inorganic particulate matter and their origins.

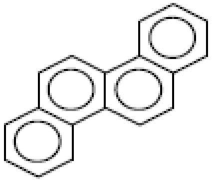
Organic Particles

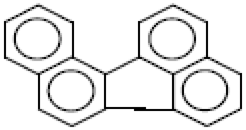
- Organic particulate matter is produced by internal combustion engines in complicated processes that involve pyrosynthesis and nitrogenous compounds.
- These products may include nitrogen-containing compounds and oxidized hydrocarbon polymers. Lubricating oil and its additives may also contribute to organic particulate matter.
- A study of particulate matter emitted by gasoline auto engines (with and without catalysts) and diesel truck engines measured more than 100 compounds quantitatively.
- Among the prominent classes of compounds found were *n*-alkanes, *n*-alkanoic acids, benzaldehydes, benzoic acids, azanaphthalenes, polycyclic aromatic hydrocarbons, oxygenated PAHs, pentacyclic triterpanes, and steranes
- (the last two classes of hydrocarbons are multiringed compounds characteristic of petroleum that enter exhaust gases from lubricating oil).

Cont.,

- Aldehydes, ketones, epoxides, peroxides, esters, quinones, and lactones are found among the oxygenated neutral components, some of which may be mutagenic or carcinogenic.
- **Polycyclic aromatic hydrocarbons (PAH) in atmospheric particles have received a great deal of attention because of the known carcinogenic effects .**
- Prominent among these compounds are benzo(a)pyrene, benz(a)anthracene, chrysene, benzo- (e)pyrene, benz(e)acephenanthrylene, benzo(j)fluoranthene, and indenol.


Benzo(a)pyrene


Chrysene


Benzo(j)fluoranthene

Fly Ash

- **Much of the mineral particulate matter in a polluted atmosphere is in the form of oxides and other compounds produced during the combustion of high-ash fossil fuel.**
- Much of the mineral matter in fossil fuels such as coal or lignite is converted during combustion to a fused, glassy bottom ash which presents no air pollution problems.
- Smaller particles of **fly ash** enter furnace flues and are efficiently collected in a properly equipped stack system. However, some fly ash escapes through the stack and enters the atmosphere.
- **Unfortunately, the fly ash thus released tends to consist of smaller particles that do the most damage to human health, plants, and visibility.**

Asbestos

- Asbestos is the name given to a group of fibrous silicate minerals, approximate formula $Mg_3P(Si_2O_5)(OH)_4$.
- The tensile strength, flexibility, and non flammability of asbestos have led to many uses including structural materials, brake linings, insulation, and pipe manufacture.
- **Most of it used for brake linings and pads, roofing products, cement/asbestos pipe, gaskets, heat-resistant packing, and specialty papers.**
- **Asbestos is of concern as an air pollutant because when inhaled it may cause asbestosis (a pneumonia condition), mesothelioma (tumor of the mesothelial tissue lining the chest cavity adjacent to the lungs), and bronchogenic carcinoma (cancer originating with the air passages in the lungs).**
- Therefore, uses of asbestos have been severely curtailed and widespread programs have been undertaken to remove the material from buildings.

3.6.1.6 Toxic metals particulates

- Some of the metals found predominantly as particulate matter in polluted atmospheres are **known to be hazardous to human health.**
- **Lead is the toxic metal of greatest concern in the urban atmosphere because it comes closest to being present at a toxic level; mercury ranks second.**
- Others include beryllium, cadmium, chromium, vanadium, nickel, and arsenic (a metalloid).

3.6.1.7. Radioactive particulates

- **Some of the radioactivity detected in atmospheric particles is of natural origin.**
- This activity includes that produced when cosmic rays act on nuclei in the atmosphere to produce radionuclides, **including 7Be, 10Be, 14C, 39Cl, 3H, 22Na, 32P, and 33P.**
- A significant **natural source of radionuclides in the atmosphere is radon, a noble gas product of radium decay.**
- Radon may enter the atmosphere as either of two isotopes, 222Rn (half-life 3.8 days) and 220Rn (half-life 54.5 seconds).

- Both are alpha emitters in decay chains that terminate with stable isotopes of lead.
- The initial decay products, 218Po and 216Po, are nongaseous and adhere readily to atmospheric particulate matter.

3. 6.1.8. Water as particulate matter

- **Droplets of water are very widespread in the atmosphere.**
- **Although a natural phenomenon, such droplets can have significant and sometimes harmful effects.**
- The most important such consequence is **reduction of visibility**, with accompanying detrimental effects on driving, flying, and boat navigation.
- **Water droplets in fog act as carriers of pollutants.**
- The most important of these are solutions of corrosive salts, particularly ammonium nitrates and sulfates, and solutions of strong acids.

3.6.1.9. Effects of particles

- **Atmospheric particles have numerous effects. The most obvious of these is reduction and distortion of visibility.**
- They **provide active surfaces upon which heterogeneous** atmospheric chemical reactions can occur, and nucleation bodies for the condensation of atmospheric water vapor, thereby exerting a significant influence upon weather and air pollution phenomena.
- The most **visible effects of aerosol particles upon air quality result from their optical effects.**
- Particles smaller than about 0.1μm in diameter **scatter light** much like molecules, that is, Rayleigh scattering.
- Generally, such particles have an insignificant effect upon visibility in the atmosphere.
- Atmospheric particles **inhaled through the respiratory** tract may damage health. Relatively large particles are likely to be retained in the nasal cavity and in the pharynx, whereas very small particles are likely to reach the lungs and be retained by them.

3.6.1.10. Control of particulate emissions

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- ☐ The removal of particulate matter from gas streams is the most widely practiced means of air pollution control.
- ☐ A number of devices have been developed for this purpose which differs widely in effectiveness, complexity, and cost.
- ☐ The selection of a particle removal system for a gaseous waste stream depends upon
  - ➢ the particle loading, nature of particles (size distribution), and
  - ➢ type of gas-scrubbing system used.

Chem 3114 for BSC Chemistry students; By Feyisa Wedajo Kumsa
fwadaajoo@gmail.com' April,2020

i) Particle Removal by Sedimentation and Inertia

- The simplest means of particulate matter removal is sedimentation.
- Gravitational settling chambers may be employed for the removal of particles from gas streams by simply settling under the influence of gravity.
- These chambers take up large amounts of space and have low collection efficiencies, particularly for small particles.
- Gravitational settling of particles is enhanced by increased particle size, which occurs spontaneously by coagulation.
- Thus, over time, the sizes of particles increase and the number of particles decreases in a mass of air that contains particles.

GRAVITY SETTLING CHAMBERS

The gravity settler was one of the first devices used to control particulate emissions. It is an expansion chamber in which the gas velocity is reduced, thus allowing the particle to settle out under the action of gravity. One primary feature of this device is that the external force causing separation of particles from the gas stream is provided free by nature. This chamber's use in industry, however, is generally limited to the removal of larger-sized particles, e.g., 40–60 µm in diameter.

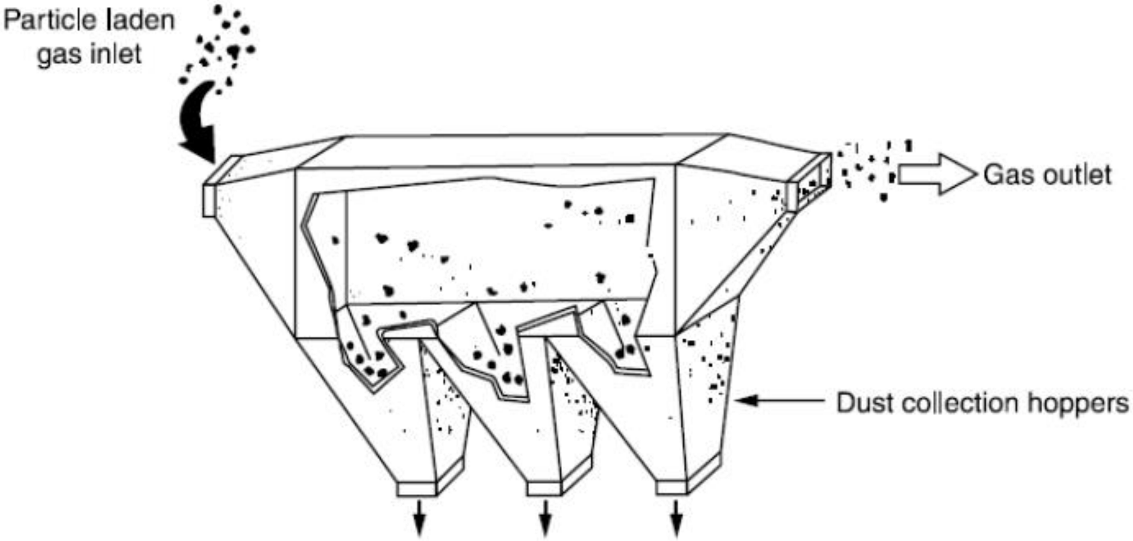

Figure 8.1 Horizontal flow settling chamber.

This chamber's use in industry, however, is generally limited to the removal of larger-sized particles, e.g., 40–60 µm in diameter.

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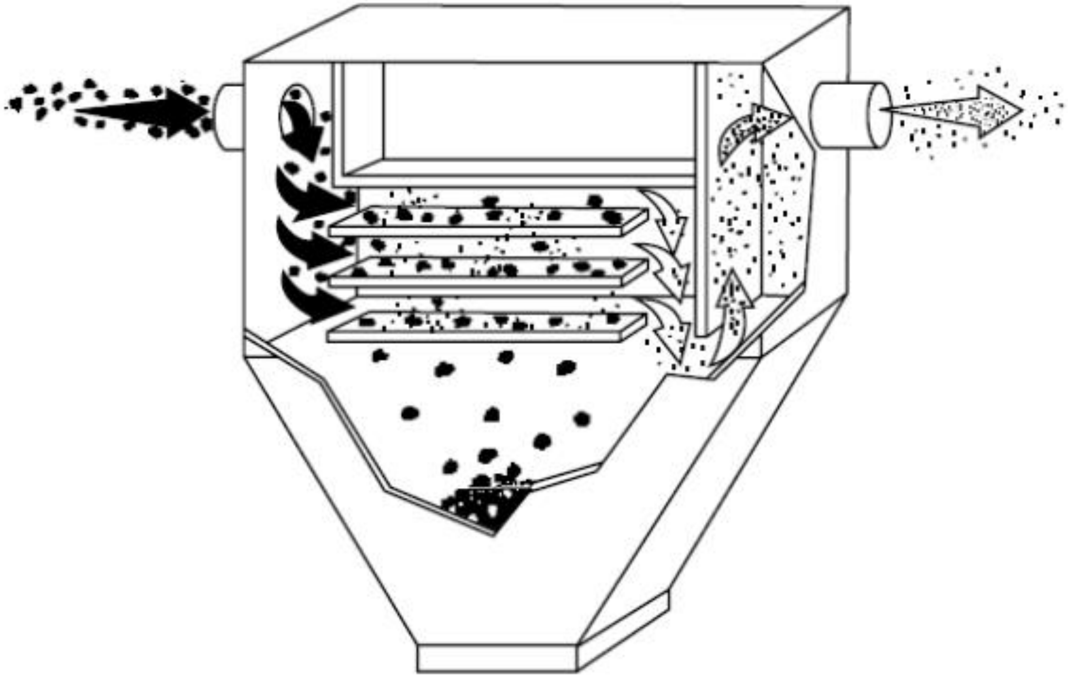


Figure 8.2 Howard settling chamber (multiple tray).

improve the collection efficiency of small particles (as small as 15 µm in diameter).

Cyclones

- Cyclones are in many size and shape.
- **Large particles impact and fall down the cyclone wall and are collected in hopper**

$$F = \frac{mv^2}{r}$$

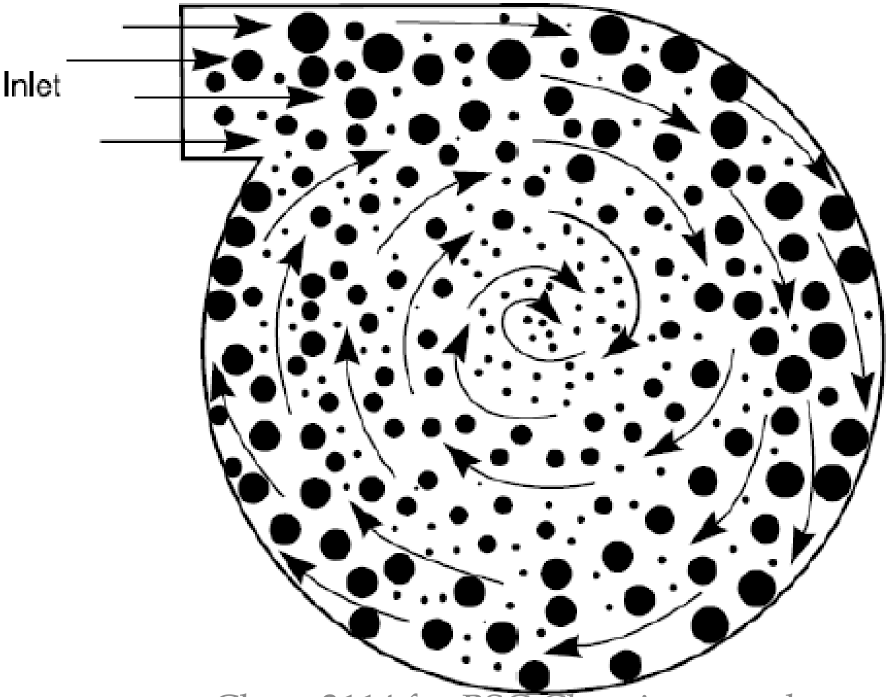
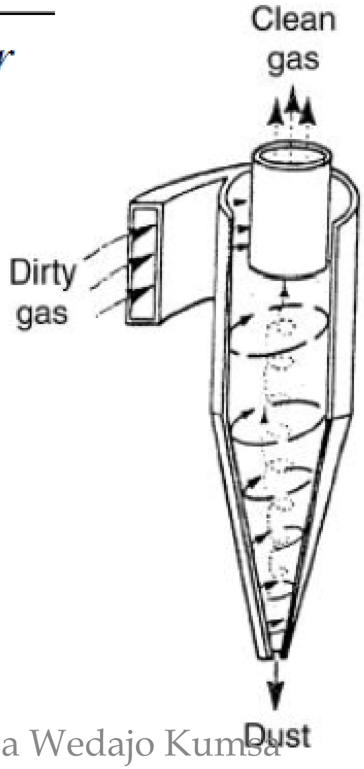


Figure 9.1 Particle collection process.



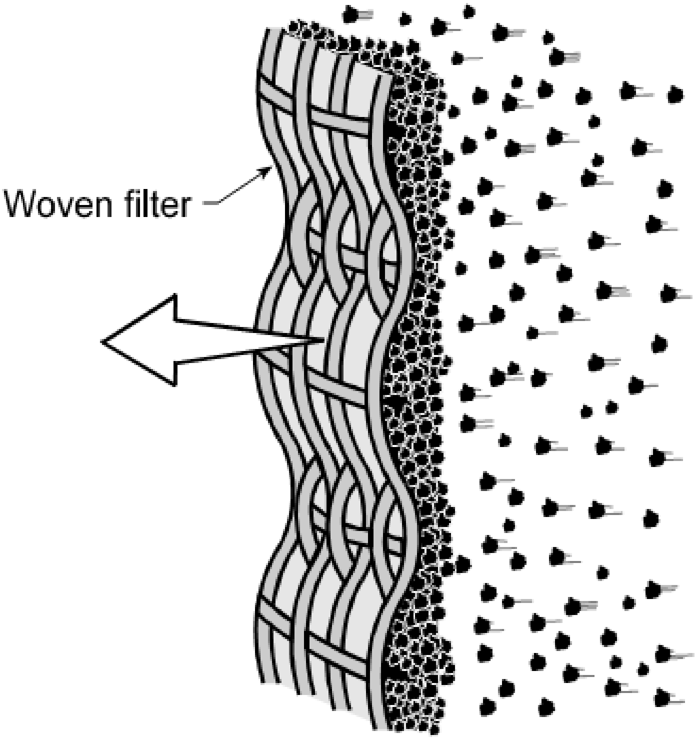
ii) Particle filtration

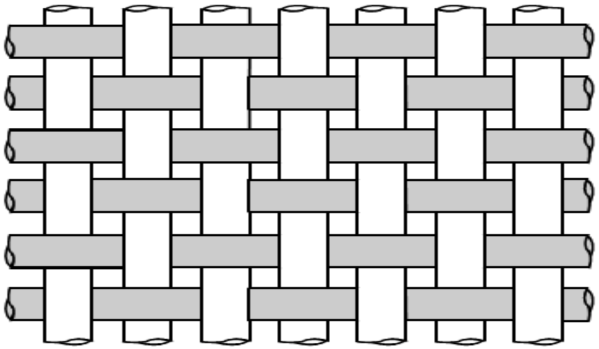
- Fabric filters, as their name implies, consist of fabrics that allow the passage of gas but retain particulate matter.
- These are used to collect dust in bags contained in structures called *baghouses*.
- Periodically, the fabric composing the filter is shaken to remove the particles and to reduce back-pressure to acceptable levels.
- Collected particulate matter is removed from bags by mechanical agitation, blowing air on the fabric, or rapid expansion and contraction of the bags.

Cont.,

- The fabric filter consist of one or more isolated compartments containing rows of fabric bags in the form of round, flat, tube, pleated cartridges.
- The particles passes along the surface of the bags then radially through fabric.
- It collect particles with sizes ranging from submicron to several hundred microns in diameter at efficiency in excess of 99%.
- the layer of dust, dust cake collected on the fabric is primarily responsible for this efficiency.

Bughouses





Scrubbers

- A scrubber is an air pollution control devices that removes PM and acids from waste gases streams of stationary point sources.

- In addition to removing particles, venturis may serve as quenchers to cool exhaust gas, and as scrubbers for pollutant gases.

SCRUBBER

- The pollutant are removed primarily through the impaction, diffusion, interception and /or absorption of the pollutant onto droplets of liquid.
- Then the liquid containing the pollutant is the collected for disposal.
- Collection efficiency for wet scrubber vary with the particle size distribution of the waste gas stream.
- Collection efficiency decreases as the PM size decreases. It ranges from greater than 99% for venturi scruber and 40-60% for simple spray towers.

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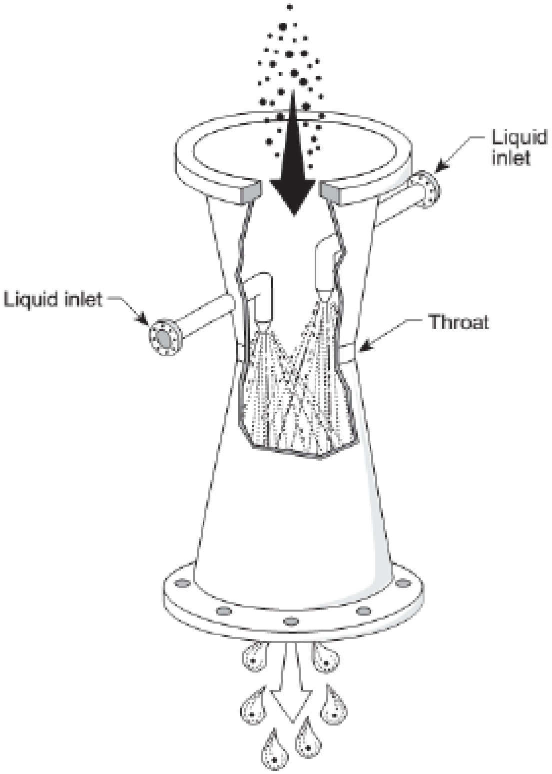
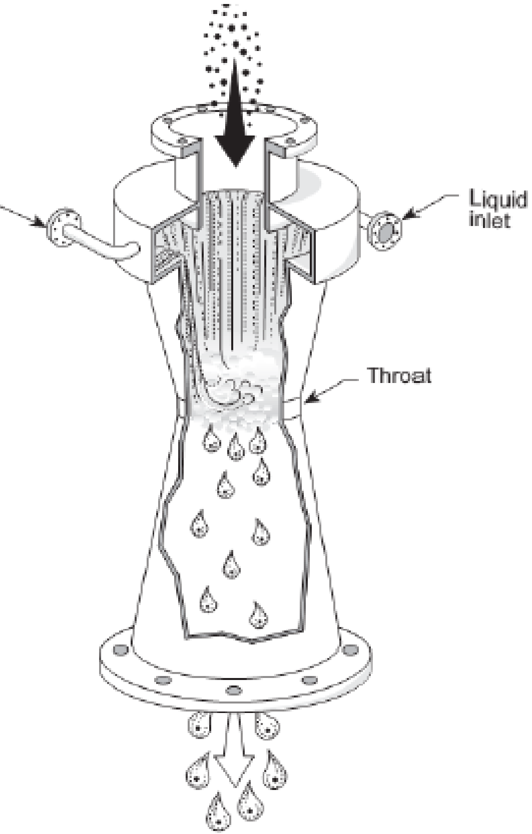
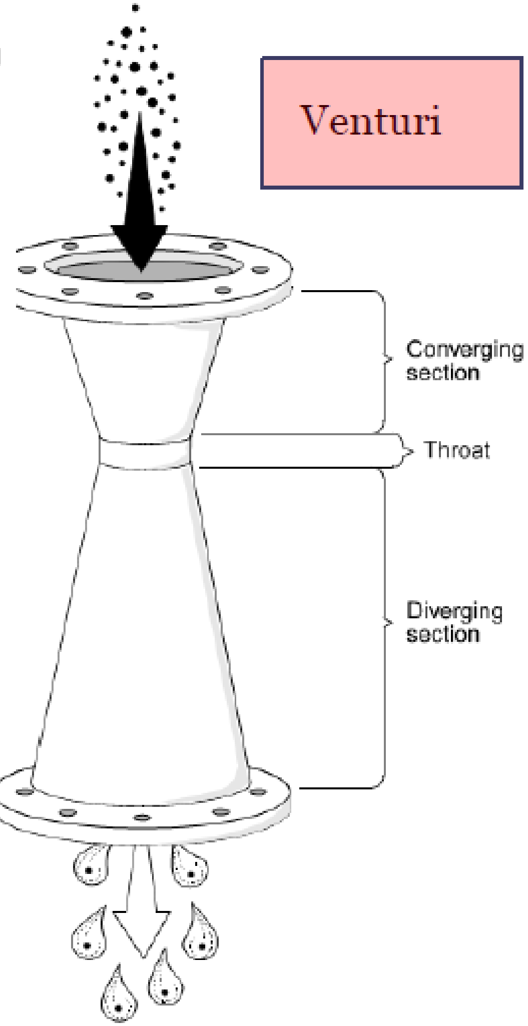
With throat sprays





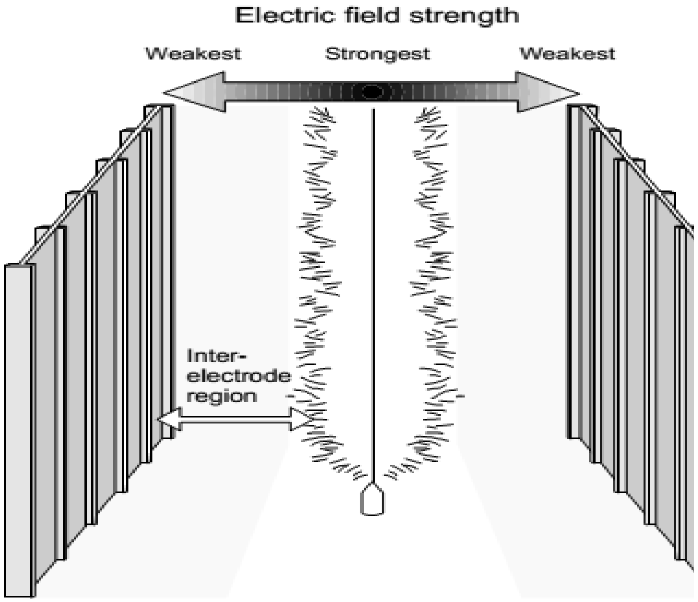
Wetted throat

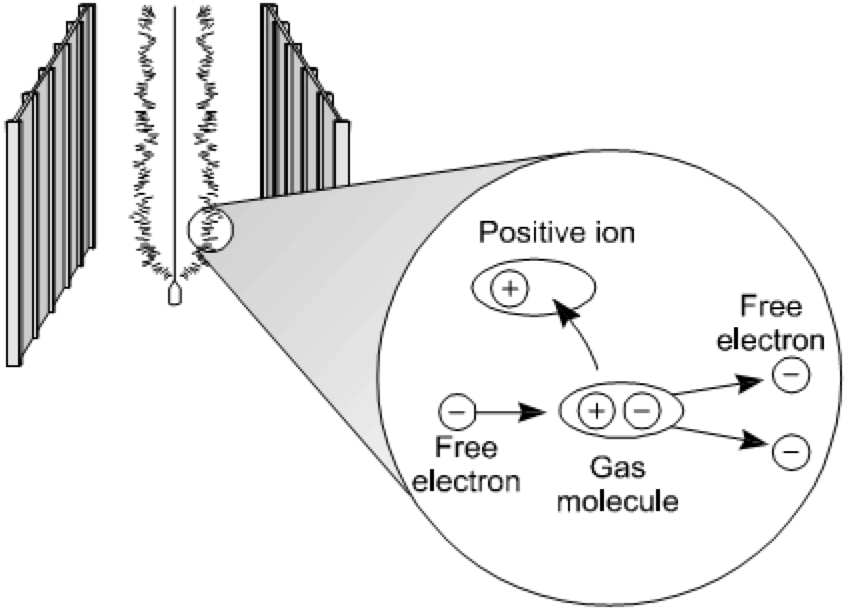
Venturi



iii: Electrostatic precipitator(ESP)

- An electrostatic precipitator(ESP) is a particle control device that uses electric forces to move the particles out of the flowing gas stream and onto collector plates.
- Some precipitators remove the particles by intermittent or continuous washing with water





3.6.2 Gaseous inorganic air pollutants

3.6.2.1 Inorganic pollutant gases

- A number of gaseous inorganic pollutants enter the atmosphere as the result of human activities.
- **Those added in the greatest quantities are CO, SO_2, NO, and NO_2 (these quantities are relatively small compared to the amount of CO_2 in the atmosphere).**
- **Other inorganic pollutant gases include NH_3, N_2O, N_2O_5, H_2S, Cl_2, HCl, and HF.**
- substantial quantities of some of these gases are added to the atmosphere each year by human activities.
- Globally, atmospheric emissions of carbon monoxide, sulfur oxides, and nitrogen oxides are of the order of one to several hundred million tons per year.

3.6.2.2 Production and control of carbon monoxide

- **Carbon monoxide, CO, causes problems in cases of locally high concentrations because of its toxicity.**
- The overall atmospheric concentration of carbon monoxide is about 0.1 ppm corresponding to a burden in the earth's atmosphere of approximately 500 million metric tons of CO with an average residence time ranging from 36 to 110 days.
- **Much of this CO is present as an intermediate in the oxidation of methane by hydrxoyl radical.**

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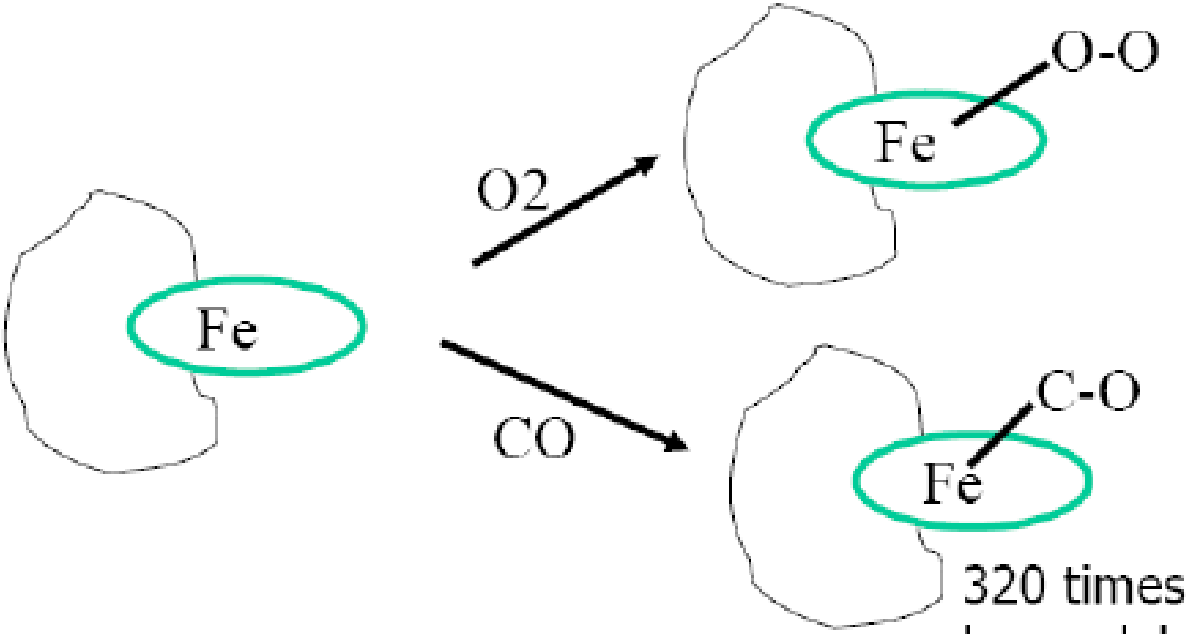
Carbon monoxide: Health effect

CO enters the blood stream and binds preferentially to hemoglobin, thereby replacing oxygen.



320 times stronger than hemoglobin-O2 binding

Cont.

Sources of carbon monoxide:

Incomplete combustion of fuel (engines of automobiles); biomass burning; methane oxidation; oxidation of various types of hydrocarbons; decay of plant matter.

Control strategies:

Employ a higher air/fuel ratio during combustion of the fuel;

Employ catalytic exhaust reactors (conversion of CO to CO_2);

Addition of oxygenates to gasoline (e.g., methanol, ethanol).

ii) Fate of atmospheric Carbon monoxide (CO)

- It is generally agreed that carbon monoxide is **removed from the atmosphere by reaction with hydroxyl radical, HO•:**
  - **$CO + HO\bullet \rightarrow CO_2 + H$**
- The reaction produces hydroperoxyl radical as a product:

  $O_2 + H + M \rightarrow HOO\bullet + M$
- HO• is regenerated from HOO• by the following reactions:

  $HOO\bullet + NO \rightarrow HO\bullet + NO_2$

  $HOO\bullet + HOO\bullet \rightarrow H_2O_2 + O_2$
- The latter reaction is followed by photochemical dissociation of H_2O_2 to regenerate HO•:

  $H_2O_2 + h\nu \rightarrow 2HO\bullet$
- Methane is also involved through the atmospheric **CO/HO•/ CH_4 cycle**.
- Soil microorganisms act to remove CO from the atmosphere. Therefore, **soil is a sink for carbon monoxide.**

3.6.2.3 Sulfur dioxide sources and the sulfur cycle

- **On a global basis, sulfur compounds enter the atmosphere to a very large extent through human activities.**
- Approximately 100 million metric tons of sulfur per year enters the global atmosphere through anthropogenic activities, **primarily as SO_2 from the combustion of coal and residual fuel.**
- The greatest uncertainties in the cycle have to do with **non-anthropogenic sulfur**, which enters the atmosphere largely as SO_2 and H_2S from **volcanoes,** and as $(CH_3)_2S$ and H_2S from the **biological decay of organic matter and reduction of sulfate.**
- The **single largest source of natural sulfur discharged to the atmosphere is now believed to be biogenic dimethyl sulfide, $(CH_3)_2S$,** from marine sources.

Sulfur cycle

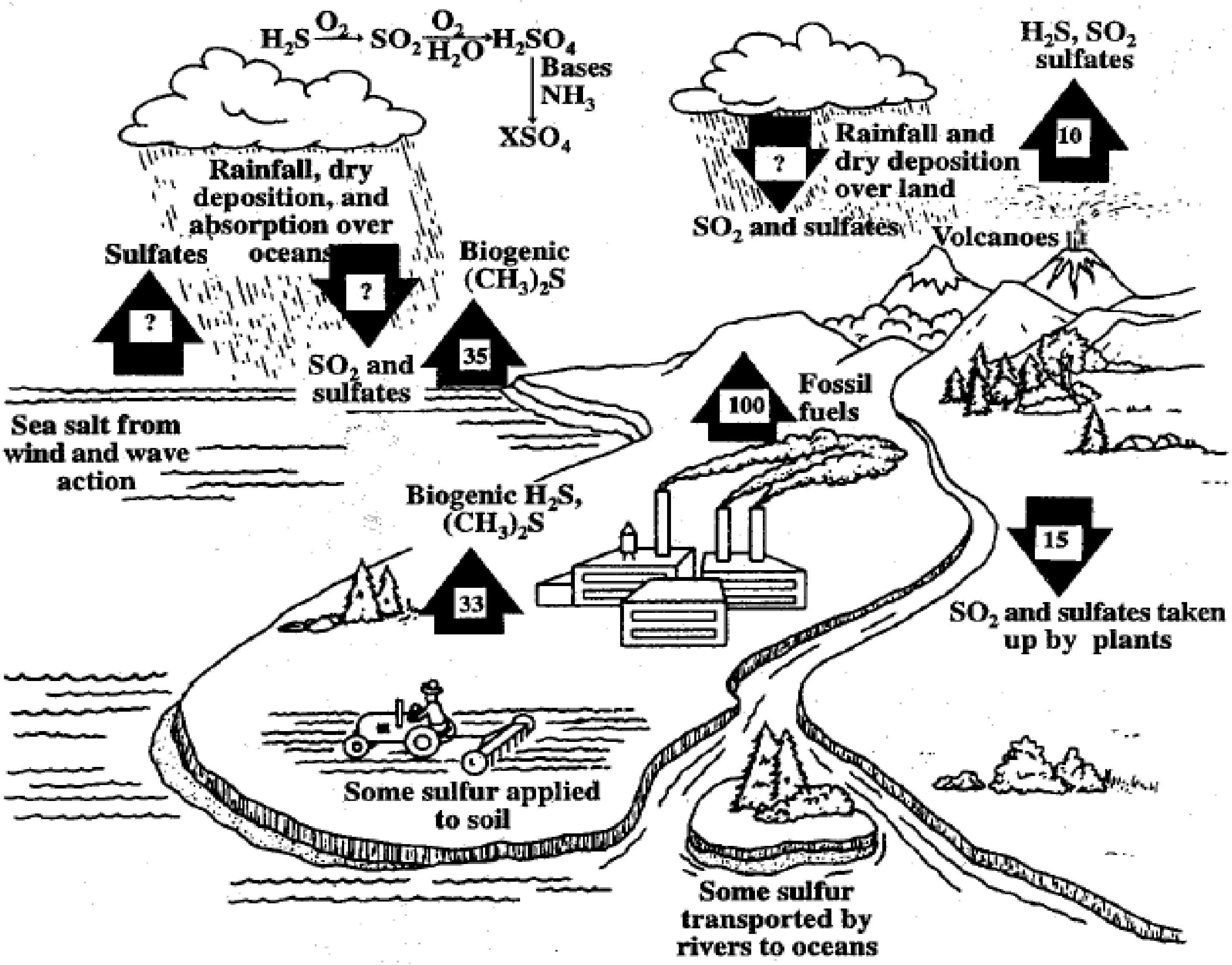


Figure 3.6.2.3 the global atmospheric sulfur cycle.

i) Sulfur dioxide reactions in the atmosphere

- Many factors, including temperature, humidity, light intensity, atmospheric transport, and surface characteristics of particulate matter, may influence the atmospheric chemical reactions of sulfur dioxide.
- Reaction products of sulfur dioxide are thought to be responsible for some aerosol formation.
- Whatever the processes involved, much of the sulfur dioxide in the atmosphere is ultimately oxidized to sulfuric acid and sulfate salts, particularly ammonium sulfate and ammonium hydrogen sulfate.

Cont.,

- Some of the possible ways in which sulfur dioxide may react in the atmosphere are:

1. Photochemical reactions;
2. Photochemical and chemical reactions in the presence of nitrogen oxides and/or hydrocarbons, particularly alkenes;
3. Chemical processes in water droplets, particularly those containing metal salts and ammonia; and
4. Reactions on solid particles in the atmosphere.

Cont.,

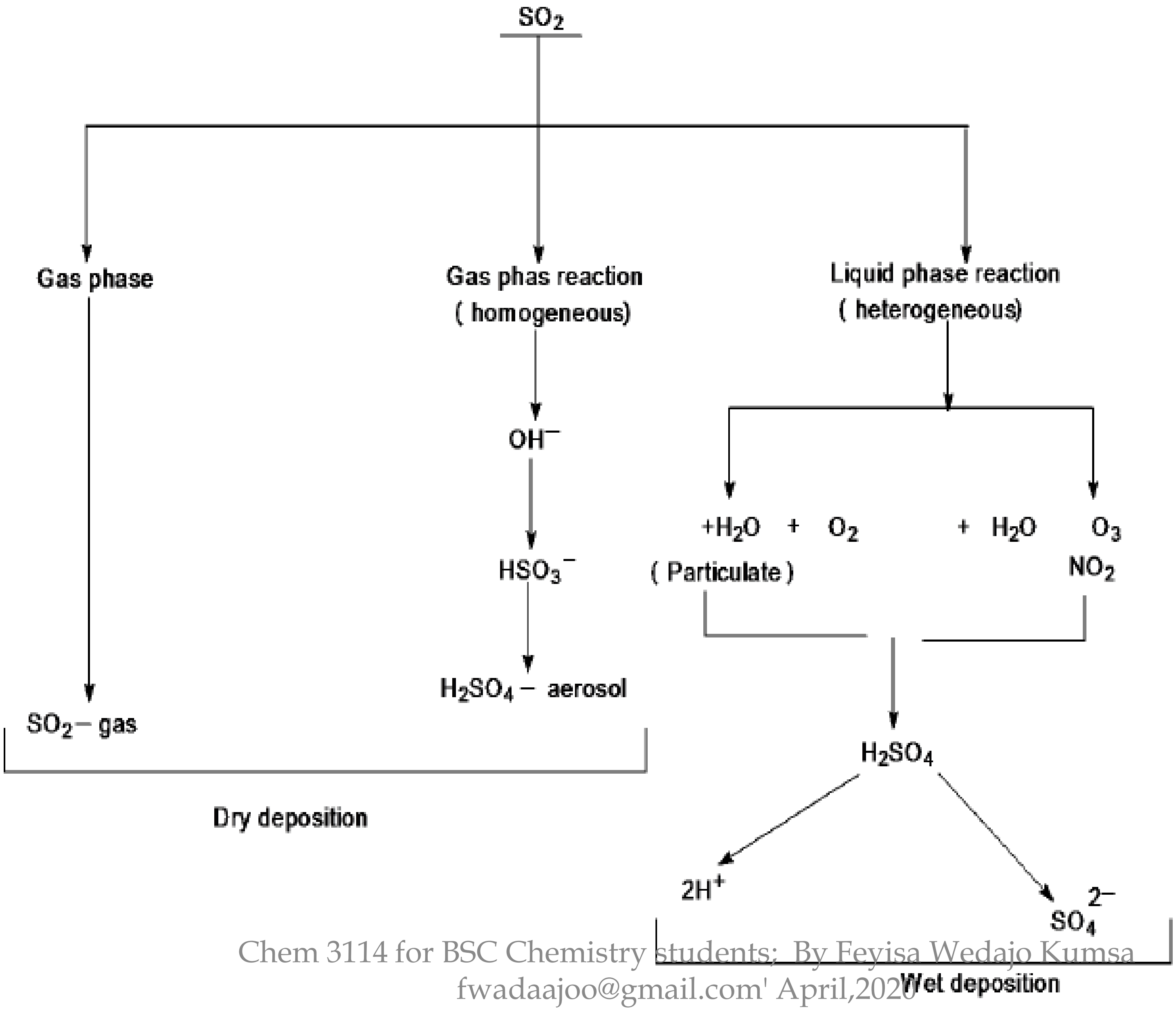
- Among the oxidizing species present which could bring about this fast reaction are:

$HO\bullet$, $HOO\bullet$, O, O_3, NO_3, N_2O_5, $ROO\bullet$, and $RO\bullet$

- The most important gas-phase reaction leading to the oxidation of SO_2 is the addition of $HO\bullet$ radical, forming a reactive free radical which is eventually converted to a form of sulfate earosol.

$$HO\bullet + SO_2 \longrightarrow HOSO_2\bullet$$

Acid deposition



SO_2

Gas phase

SO_2 – gas

Gas phas reaction (homogeneous)

OH^-

HSO_3^-

H_2SO_4 – aerosol

Dry deposition

Liquid phase reaction (heterogeneous)

$+H_2O$ + O_2 (Particulate)

+ H_2O O_3 NO_2

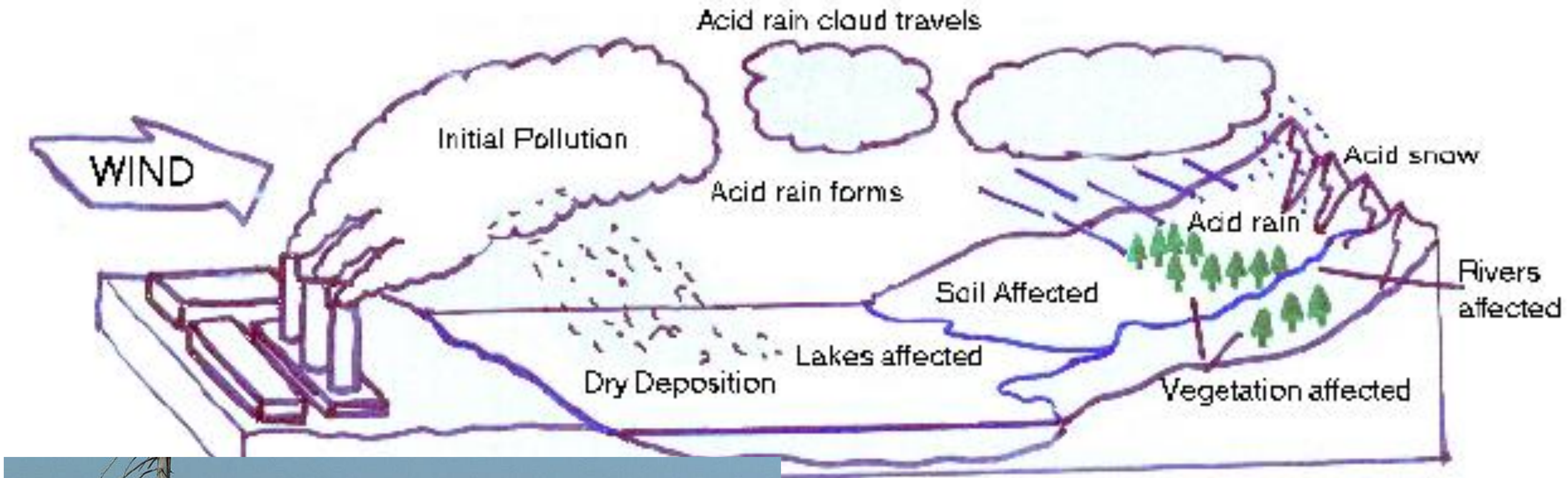
H_2SO_4

$2H^+$

SO_4^{2-}

Wet deposition

Acid rain


Acid rain cloud travels
WIND
Initial Pollution
Acid rain forms
Acid snow
Acid rain
Soil Affected
Rivers affected
Lakes affected
Dry Deposition
Vegetation affected

iii) Sulfur dioxide removal

- A number of processes are being used to remove sulfur and sulfur oxides from fuel before combustion and from stack gas after combustion.
- Most of these efforts concentrate on coal, since it is the major source of sulfur oxides pollution.

1. Physical separation techniques may be used to remove discrete particles of pyritic sulfur from coal.
2. Chemical methods may also be employed for removal of sulfur from coal.

- Fluidized bed combustion of coal promises to eliminate SO_2 emissions at the point of combustion.
- The process consists of burning granular coal in a bed of finely divided limestone or dolomite maintained in a fluid-like condition by air injection.
- Heat calcines the limestone, $CaCO_3 \rightarrow CaO + CO_2$ and the lime produced absorbs SO_2:

$$CaO + SO_2 \rightarrow CaSO_3 \text{ (Which may be oxidized to } CaSO_4\text{)}$$

3.6.2.4 Nitrogen oxides in the atmosphere

- The three oxides of nitrogen normally encountered in the atmosphere are nitrous oxide (N_2O), nitric oxide (NO), and nitrogen dioxide (NO_2).
- Nitrous oxide, a commonly used anesthetic known as —laughing gas, is produced by microbiological processes and is a component of the unpolluted atmosphere at a level of approximately 0.3 ppm.
- This gas is relatively unreactive and probably does not significantly influence important chemical reactions in the lower atmosphere.
- Its concentration decreases rapidly with altitude in the stratosphere due to the photochemical reaction $N_2O + h\nu \rightarrow N_2 + O$ and some reaction with singlet atomic oxygen:

$$N_2O + O \rightarrow N_2 + O_2 \qquad \text{and} \qquad N_2O + O \rightarrow 2NO$$

- These reactions are significant in terms of depletion of the ozone layer.
- Increased global fixation of nitrogen, accompanied by increased microbial production of N_2O, could contribute to ozone layer depletion.
- Colorless, odorless nitric oxide (NO) and pungent red-brown nitrogen dioxide (NO_2) are very important in polluted air.

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- The latter are much more significant because of regionally high NO_2 concentrations which can cause severe air quality deterioration.
- Practically all anthropogenic NO_x enters the atmosphere as a result of the combustion of fossil fuels in both stationary and mobile sources.

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- Nitrogen dioxide is a very reactive and significant species in the atmosphere.
- It absorbs light throughout the ultraviolet and visible spectrum penetrating the troposphere.
- At wavelengths below 398 nm, photo dissociation occurs, $NO_2 + h\nu \rightarrow NO + O$

  to produce ground state oxygen atoms.

Cont.,

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- Dinitrogen pentoxide formed in the above reaction is the anhydride of nitric acid, which it forms by reacting with water: $N_2O_5 + H_2O \rightarrow 2HNO_3$
- In the stratosphere, nitrogen dioxide reacts with hydroxyl radicals to produce nitric acid:

$$HO\bullet + NO_2 \rightarrow HNO_3$$

- In this region, the nitric acid can also be destroyed by hydroxyl radicals, $HO\bullet + HNO_3 \rightarrow H_2O + NO_3$ or
- by a photochemical reaction, $HNO_3 + h\nu \rightarrow HO\bullet + NO_2$
- so that HNO_3 serves as a temporary sink for NO_2 in the stratosphere.
- Nitric acid produced from NO_2 is removed as precipitation, or reacts with bases (ammonia, particulate lime) to produce particulate nitrates.

ii) Harmful Effects of Nitrogen Oxides

- Nitric oxide, NO, is less toxic than NO_2. Like carbon monoxide and nitrite, NO attaches to hemoglobin and reduces oxygen transport efficiency.
- Acute exposure to NO_2 can be quite harmful to human health.
- Nitrogen oxides are known to cause fading of dyes and inks used in some textiles.
- Much of the damage to materials caused by NO_x comes from secondary nitrates and nitric acid.
- results in a net reaction for the destruction of ozone:

$$NO_2 + O \rightarrow NO + O_2$$

$$O + O_3 \rightarrow O_2 + O_2$$

- Along with NO_x, water vapor is also emitted into the atmosphere by aircraft exhausts, which could accelerate ozone depletion by the following two reactions:

$$O + H_2O \rightarrow HO\bullet + HO\bullet$$

$$HO\bullet + O_3 \rightarrow HOO\bullet + O_2$$

iii) Control of Nitrogen Oxides

- The level of NOx emitted from stationary sources such as power plant furnaces generally falls within the range of 50-1000 ppm.

- ☐ Reduction of flame temperature to prevent NO formation is accomplished by adding recirculated exhaust gas, cool air, or inert gases.

3.6.2.5 Ammonia in the atmosphere

- Ammonia is present even in unpolluted air as a result of natural biochemical and chemical processes.
- Among the various **sources** of atmospheric ammonia are **microorganisms, decay of animal wastes, sewage treatment, coke manufacture, ammonia manufacture,** and leakage from ammonia-based refrigeration systems.
- Ammonia is removed from the atmosphere by its affinity for water and by its action as a base.
- It is a key species in the formation and neutralization of nitrate and sulfate aerosols in polluted atmospheres.
- Ammonia reacts with these acidic aerosols to form ammonium salts:

$NH_3 + HNO_3 \rightarrow NH_4NO_3$, $NH_3 + H_2SO_4 \rightarrow NH_4HSO_4$

- Ammonium salts are among the more corrosive salts in atmospheric aerosols.

3.6.3 Gaseous organic air pollutants

Effect of Organic pollutants

- Organic pollutants may have a strong effect upon atmospheric quality.
- The effects of organic pollutants in the atmosphere may be divided into <u>two major categories</u>.
- The first consists of **direct effects**, such as cancer caused by exposure to vinyl chloride.
- The second is the formation of **secondary pollutants**, especially photochemical smog. In the case of pollutant hydrocarbons in the atmosphere, the latter is the more important effect.
- In some localized situations, particularly the workplace, direct effects of organic air pollutants may be equally important.

Removal of Organic Substances from the Atmosphere

- Organic contaminants are lost from the atmosphere by a number of routes.
- These include :
  - <u>dissolution in precipitation (rainwater</u>),
  - dry deposition,
  - <u>photochemical reactions</u>,
  - formation of and incorporation into particulate matter, and
  - <u>uptake by plants</u>.
- For example; forest trees present a large surface area to the atmosphere and are particularly important in filtering organic contaminants from air.

Cont.,

- As a result, the least volatile persistent organic pollutants are deposited near their sources, those of **relatively high volatility are distilled into Polar Regions,** **and those of** **intermediate volatility are deposited predominantly at mid latitudes.**
- This phenomenon has some important implications regarding the **accumulation of persistent organic pollutants in environmentally fragile polar regions** far from industrial sources.

3.6.3.7 Organohalide compounds

- **Organohalides:** consist of halogen-substituted hydrocarbon molecules, each of which contains at least one atom of F, Cl, Br, or I.
- They may be saturated (**alkyl halides**), unsaturated (**alkenyl halides**), or aryl (**aryl halides)**.
- Although most organohalide compounds of pollution concern are from anthropogenic sources, it is now known that a **large variety of such compounds are generated by organisms, particularly those in marine environments.**
- **Chloromethane** is produced by marine/ocean algae, forest fires, brush fires, volcanoes.

i) Chloro carbon compound (Chlorinated hydrocarbons)

- Volatile **chloromethane** (methyl chloride) is consumed in the manufacture of silicones.
- **Dichloromethane** is a volatile liquid with excellent solvent properties for nonpolar organic solutes.
- It has been used as a solvent for the decaffeination of coffee, in paint strippers, as a blowing agent in urethane polymer manufacture, and to depress vapor pressure in aerosol formulations.

Cont.,

- **Vinyl chloride** is consumed in large quantities as a raw material to manufacture pipe, hose, wrapping, and other products fabricated from polyvinyl chloride plastic.
  - This highly flammable, volatile, sweet-smelling gas is known to cause angiosarcoma, a rare form of liver cancer.
- **Trichloroethylene** is a clear, colorless, nonflammable, volatile liquid.
  - It is an excellent degreasing and dry-cleaning solvent, and has been used as a household solvent and for food extraction (for example, in decaffeination of coffee).
- **Allyl chloride** is an intermediate in the manufacture of allyl alcohol and other allyl compounds, including pharmaceuticals, insecticides, and thermosetting varnish and plastic resins.

ii) Chlorofluorocarbons

- **Dichlorodifluoromethane** is one of the chlorofluorocarbon compounds once widely manufactured as a refrigerant and involved in stratospheric ozone depletion.
- One of the more common industrial chlorinated solvents is **1,1,1-trichloroethane**.
- Viewed as halogen-substituted derivatives of alkenes, the **alkenyl** or **olefinic organohalides** contain at least one halogen atom and at least one carbon-carbon double bond.
- The most significant of these are the lighter chlorinated compounds.
- **Chlorofluorocarbons** (**CFC**s), such as dichlorodifluoromethane, commonly called Freons, are volatile 1- and 2-carbon compounds that contain Cl and F bonded to carbon.
- These compounds are notably stable and nontoxic.
- They have been widely used in recent decades in the fabrication of **flexible and rigid foams and as fluids for refrigeration and air conditioning.**
- The most widely manufactured of these compounds are :

CCl_3F (CFC-11, bp 24°C), CCl2F2 (CFC-12, bp - 28°C),
C2Cl$_3$F3 (CFC-113), C_2Cl_2F4 (CFC-114), and C_2ClF_5 (CFC-115).

So Freon's have the following property

- Inert in most chemical reactions
- Stable at higher temperatures and towards acids and bases
- Nonflammable
- Nontoxic

❑Thus it serve as alternative/substituent for ammonia as refrigerant, due to NH3 is an aggressive and toxic chemicals

3.6.4 The endangered global atmosphere

- **Anthropogenic change in the atmosphere**
  - There is a very strong connection between life forms on earth and the nature of earth's climate, which determines its suitability for life.
- **The effects of human activities and the anthrosphere on the atmosphere are summarized below:**

1. **Industrial activities, which emit** a variety of atmospheric pollutants including SO_2, particulate matter, photochemically reactive hydrocarbons, chlorofluorocarbons, and inorganic substances (such as toxic heavy metals)

Cont.,

2. **Burning of large quantities of fossil fuel,** which can introduce CO_2, CO, SO_2, NO_x, hydrocarbons (including CH_4), and particulate soot, polycyclic aromatic hydrocarbons, and fly ash into the atmosphere
3. **Transportation practices, which emit CO_2, CO, NO_x, photochemically reactive (smog forming) hydrocarbons**, and polycyclic aromatic hydrocarbons
4. **Alteration of land surfaces, including deforestation**
5. **Burning of biomass and vegetation, including tropical and subtropical forests and savanna grasses, which produces atmospheric CO_2, CO, NO_x**, and particulate soot and polycyclic aromatic hydrocarbons
6. **Agricultural practices, which produce methane (from the digestive tracts of domestic animals and from the cultivation of rice in waterlogged anaerobic soils) and N_2O from bacterial denitrification of nitrate-fertilized soils.**

- These kinds of human activities have significantly altered the atmosphere, particularly in regard to its composition of minor constituents and trace gases.

Major effects have been the following:

- Increased acidity in the atmosphere
- Production of pollutant oxidants in localized areas of the lower troposphere
- Elevated levels of infrared-absorbing gases (greenhouse gases)
- Threats to the ultraviolet-filtering ozone layer in the stratosphere
- Increased corrosion of materials induced by atmospheric pollutants

3.6.4.1 Greenhouse gases and global warming

- ❑Do you know some of the causes for Greenhouse gases and global warming?

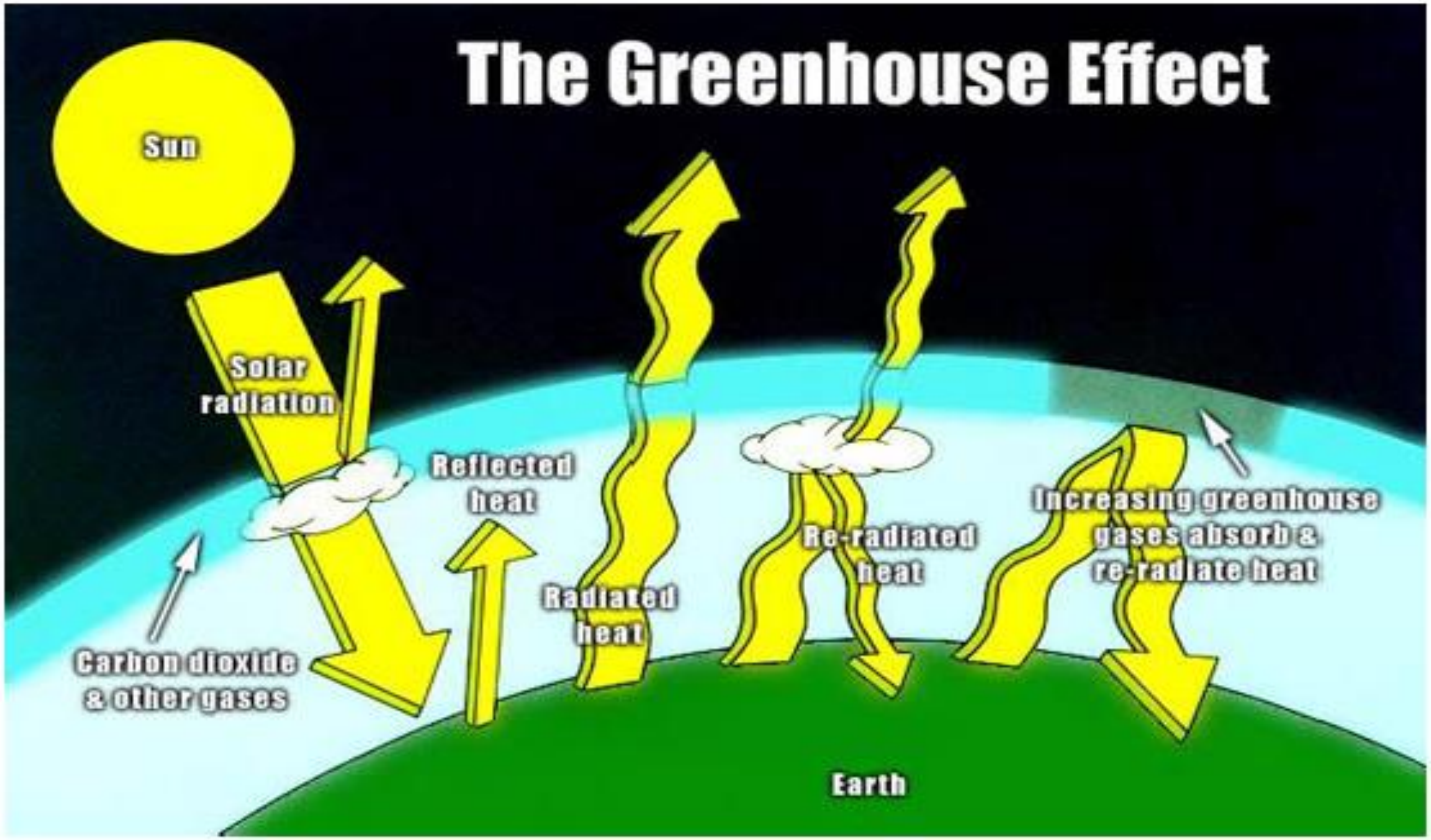
1. Mention the major greenhouse gases?
2. Mention the major effects of greenhouse gases?
3. Explain how a greenhouse gases cause global warming?
4. Explain how global warming can be minimized?

Greenhouse gases and global warming?

- ***Infrared-absorbing trace gases (other than water vapor) in the atmosphere that contribute to global warming***.
- These gases produce a ***"greenhouse effect"*** by **allowing incoming solar radiant energy to penetrate to the earth's surface while reabsorbing infrared radiation emanating** from it
- Levels of these ―greenhouse gases have increased at a rapid rate during recent decades and are continuing to do so.

Greenhouse effect

The greenhouse effect is the process in which the emission of infrared radiation by the atmosphere warms a planet's surface.



Major greenhouse gases in the atmosphere → **CO_2, H_2O, CH_4, N_2O, O_3, CFCs, SF_6**

Characteristics of greenhouse gases:

- They are able to absorb infrared light.
- These gases have molecular structure (monoatomic gases such as Ar cannot absorb infrared light.
- Their molecular vibrations must be non-symmetric, i.e., infrared active.

CO_2 positive and negative feedback mechanisms

- Forests, which have a high CO2-fixing ability. photosynthesis, grow faster and take up more CO2
- However, higher atmospheric CO2 concentrations will result in accelerated sorption of the gas by oceans. lowering of ocean water pH that will result impact organsims live in ocean water
- Warmer conditions would accelerate release of both CO_2 and CH_4 by microbial degradation of organic matter.
- Global warming might speed up the rates at which biodegradation adds these gases to the atmosphere.

Cont.,

- warming induces formation of more clouds, Clouds both reflect incoming light radiation and absorb outgoing infrared radiation,
- Drought is one of the most serious problems that could arise from major climatic change resulting from greenhouse warming.
- Typically, a three-degree warming would be accompanied by a ten percent decrease in precipitation.
- Water shortages and increased evaporation as well, decreased runoff, reducing water available for agricultural, municipal, and industrial use.
- Water shortages, in turn, lead to increased demand for irrigation and to the production of lower quality, higher salinity runoff water and wastewater.

Cont.,

- effect of warming on plant and animal pests —insects, weeds, diseases, and rodents. Many of these would certainly thrive much better under warmer conditions.

- ☐ Interestingly, another air pollutant, acid-rain-forming sulfur dioxide, may have a counteracting effect on greenhouse gases.

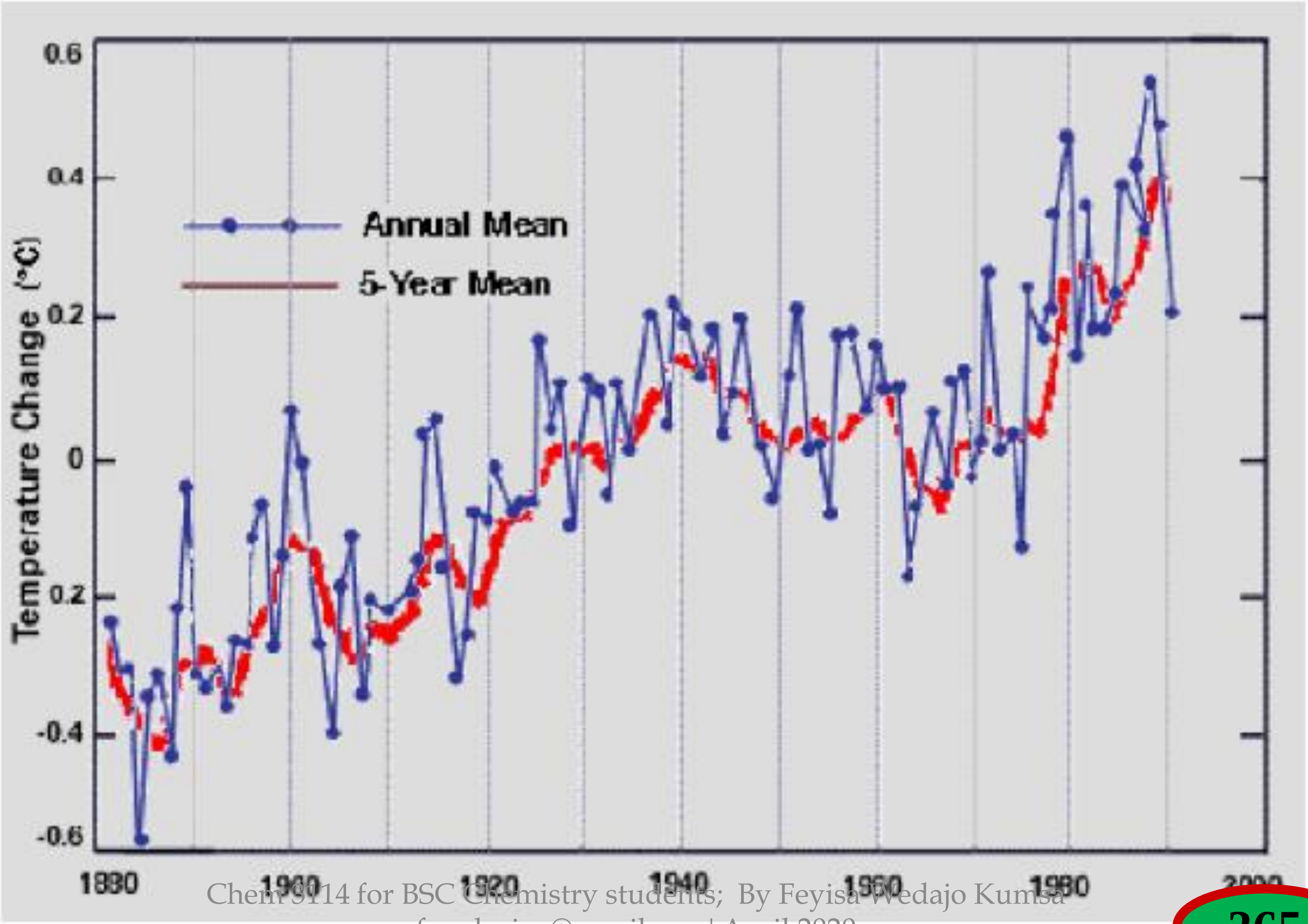
- ☐ This is because sulfur dioxide is oxidized in the atmosphere to sulfuric acid, forming a light-reflecting haze.

- ☐ Furthermore, the sulfuric acid and resulting sulfates act as condensation nuclei upon which atmospheric water vapor condenses, thereby increasing the extent, density, and brightness of light-reflecting cloud cover.

Cont.,

- Global warming is caused by a variety of gases and materials in our atmosphere; including huge amounts of carbon dioxide and methane from human activities such as extracting and burning fossil fuels, and clearing forests.
- These gases can trap heat in the atmosphere, causing steadily increasing t

Avearge Global Temperature



Global Warming Solutions: Reduce Emissions

[redacted]

In order to effectively address global warming, we must significantly **reduce the amount of heat-trapping emissions we are putting into the atmosphere.**

Cont.,

- Reduce our personal carbon emissions.
- Expand the use of renewable energy and transform our energy system to one that is cleaner and less dependent on coal and other fossil fuels.
- Increase vehicle fuel efficiency and support other solutions that reduce U.S. oil use.
- Place limits on the amount of carbon that polluters are allowed to emit.
- Build a clean energy economy by investing in efficient energy technologies, industries, and approaches.
- Reduce tropical deforestation and its associated global warming emissions.

How to reduce Global warming?

- ☐ Reduce Fossil Fuel Use.
- ✓ Burning fossil fuels increases the levels of greenhouse gases in the atmosphere. ...
- ☐ Plant Trees.
- ✓ Because carbon dioxide is the most important greenhouse gas, planting trees and other plants can slow or stop global warming. ...
- ☐ Reduce Waste
- ☐ Conserve Water
- ☐ **Sustainable Development and Climate Change**

The Clean Power Plan: a climate game changer

International climate negotiations

3.6.4.3 The Nuclear winter

- **Nuclear winter is a term used to describe a catastrophic atmospheric effect that might occur after a massive exchange of nuclear firepower between major powers.**
- The heat from the nuclear blasts and from resulting fires would cause powerful updrafts carrying sooty combustion products to stratospheric regions.
- This would result in several years of much lower temperatures and freezing temperatures even during summertime.

Nuclear winter

- is the severe global-climatic-cooling-effect, hypothesized to occur after the ignition of a number of firestorms.
- Such fires, which can inject soot into the stratosphere, have historically occurred in a number of cities, with nuclear winter researchers using both Hamburg and the less ferocious Hiroshima firestorms as the principal examples

3.6.4.4 Acid rain

1) What is Acid rain?
2) Explain the source of Acid rain.
3) Describe the effects of Acid rain.
4) Explain whether acid rain is local, regional or global pollution problem
5) Explain how Acid rain can be minimized

Acid rain

- much of the sulfur and nitrogen oxides entering the atmosphere are converted to sulfuric and nitric acids, respectively.
- When combined with hydrochloric acid arising from hydrogen chloride emissions, these acids cause acidic precipitation (acid rain) that is now a major pollution problem in some areas.
- Headwater streams and high-altitude lakes are especially susceptible to the effects of acid rain and may sustain loss of fish and other aquatic life.
- Other effects of acid rain include reductions in forest and crop productivity; leaching of nutrient cations and heavy metals from soils, rocks, and the sediments of lakes and streams; dissolution of metals such as lead and copper from water distribution pipes; corrosion of exposed metal; and dissolution of the surfaces of limestone buildings and monuments.
- As a result of its widespread distribution and effects, acid rain is an air pollutant that may pose a threat to the global atmospher

Cont.,

- Precipitation made acidic by the presence of acids stronger than CO2 (*aq*) is commonly called acid rain; the term applies to all kinds of acidic aqueous precipitation, including fog, dew, snow, and sleet.
- In a more general sense, acid deposition refers to the deposition on the earth‘s surface of aqueous acids, acid gases (such as SO2), and acidic salts (such as NH4HSO4).
- According to this definition, deposition in solution form is *acid precipitation*, and deposition of dry gases and compounds is *dry deposition*.
- Although carbon dioxide is present at higher levels in the atmosphere, sulfur dioxide, SO2, contributes more to the acidity of precipitation for two reasons.

Cont.,

☐ Gases such as HCl gas or sulfuric acid mist, most of it is a secondary air pollutant produced by the atmospheric oxidation of acid-forming gases such as the following:

- **$SO_2 + 1/2O_2 + H_2O$; Overall reaction consisting of several steps $\{2H^+ + SO_4^{2-}\}$ (*aq*)**
- **$2NO_2 + 1/2O_2 + H_2O$; Overall reaction consisting of several steps $2\{H^+ + NO_3^-\}$ (*aq*)**

❖ Chemical reactions such as these play a dominant role in determining the nature, transport, and fate of acid precipitation.

❖ As the result of such reactions the chemical properties (acidity, ability to react with other substances) and physical properties (volatility, solubility) of acidic atmospheric pollutants are altered drastically.

Scale of acid rain

- Acid rain spreads out over areas of several hundred to several thousand kilometers.
- This classifies it as a ***regional air pollution problem*** compared to a *local* air pollution problem for smog and a *global* one for ozone-destroying chlorofluorocarbons and greenhouse gases.
- Other examples of regional air pollution problems are those caused by soot, smoke, and fly ash from combustion sources and fires (forest fires).

major effects of acid rain is summarized as follows

- ☐ Direct phytotoxicity to plants from excessive acid concentrations.
- ☐ Phytotoxicity from acid-forming gases, particularly SO2 and NO2 that accompany acid rain
- ☐ Indirect phytotoxicity, such as from Al3+ liberated from soil
- ☐ Destruction of sensitive forests
- ☐ Respiratory effects on humans and other animals
- ☐ Acidification of lake water with toxic effects to Lake Flora and fauna, especially fish fingerlings

Cont.,

- Corrosion of exposed structures, electrical relays, equipment, and ornamental materials.
- Because of the effect of hydrogen ion,

$$2H^+ + CaCO_3(s) \rightarrow Ca^{2+} + CO_2\ (g) + H_2O$$

limestone, $CaCO_3$, is especially susceptible to damage from acid rain

- Associated effects, such as reduction of visibility by sulfate aerosols and the influence of sulfate aerosols on physical and optical properties of clouds.
- A significant association exists between acidic sulfate in the atmosphere and haziness.
- Soil sensitivity to acid precipitation can be estimated from cation exchange capacity.

The measures to be taken to keep the global atmosphere from danger are:

- **Minimization** by reducing emissions of greenhouse gases, switching to alternate energy sources, increasing energy conservation, and reversing deforestation.
- **Counteracting measures**, such as injecting light-reflecting particles into the upper atmosphere.
- **Adaptation**, particularly through increased efficiency and flexibility of the distribution and use of water, which might be in very short supply in many parts of the world as a consequence of greenhouse warming.

JIMMA UNIVERSITY
COLLEGE OF NATURAL SCIENCE
DEPARTMENT OF CHEMISTRY

❑Environmental chemistry and Toxicology (**Chem 3114).**

➢Course to be offered; to Chemistry BSc students

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Chapter 5

- **ENVIRONMENTAL TOXICITY AND TOXICOLOGY**

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Introduction to Toxicity and Toxicology

To understand toxicological chemistry,

- **it is essential to have some understanding of biochemistry, the science that deals with chemical processes and materials in living systems.**

Cont.,

- Research into toxic effects of substances on humans can be traced back to ancient centres of civilisation
- Chemical substances have been known to be and/or used as poison or sometimes medicines
- Toxicology has been defined as «science of the poisons»
- *"All things are poison and nothing is without poison; only the dose makes a thing not a poison" (Paracelsus)*

Toxicity

- **Toxicity: is the magnitude of adverse effects caused by a chemical**

- It is assumed that effects are produced through an interaction with the substance at a target site

- Most pollutants and hazardous substances are of concern because of their toxic effects.

- **This includes both:**

  - Long-term **chronic effects** from continual or periodic exposures to low levels of toxicants and

  - **Acute effects** from a single large exposure.

Toxicology

- ***Toxicology is the science of poisons.***
- **A poison, or toxicant**, is a substance that is harmful to living organisms because of its detrimental effects on tissues, organs, or biological processes.
- Toxicants to which subjects **are exposed** in the environment or occupationally may be in several different physical forms, such as:
  - **vapors or dusts** that are **inhaled**,
  - **liquids** that can be **absorbed through** the skin or solids ingested orally.

Cont.,

- A substance with which the toxicant may be associated **(the solvent in which it is dissolved or the solid medium in which it is dispersed) is called the matrix.** The matrix may have a strong effect upon the toxicity of the toxicant.
- **There are numerous variables related to the ways in which organisms are exposed to toxic substances.**
- One of the most crucial is **dose.**
- Another important factor is the **toxicant concentration**, which may range from the pure substance (100%) down to a very dilute solution of a highly potent poison.
- Both the **duration of exposure per incident and the frequency of exposure are** important.
- The **rate of exposure and the total time period over** which the organism is exposed are both important situational variables.
- The **exposure site and route** also affect toxicity.

Exposures are classified in to four general categories.

1. **Acute local exposure** occurs at a specific location over a time period of a few seconds to a few hours and may affect the exposure site, particularly the skin, eyes, or mucous membranes.
2. The same parts of the body can be affected by **chronic local exposure**, for which the time span may be as long as several years.
3. **Acute systemic exposure** is a brief exposure or exposure to a single dose and occurs with toxicants that can enter the body and affect organs that are remote from the entry site.
4. **Chronic systemic exposure** differs in that the exposure occurs over a prolonged time period.

Major routes for toxicants

- The major routes of accidental or intentional exposure to toxicants in humans and other animals are

- **Skin (percutaneous route),**
  - Absorption through **the skin** is most likely for liquids, solutes in solution, and semisolids, such as sludges.

- **Lungs** (inhalation, respiration, pulmonary route)
  - The **pulmonary system** is most likely to take in toxic gases or very fine, respirable solid or liquid particles.

- **Mouth (oral route).**
  - In other than a respirable form, a solid usually enters the body **orally.**

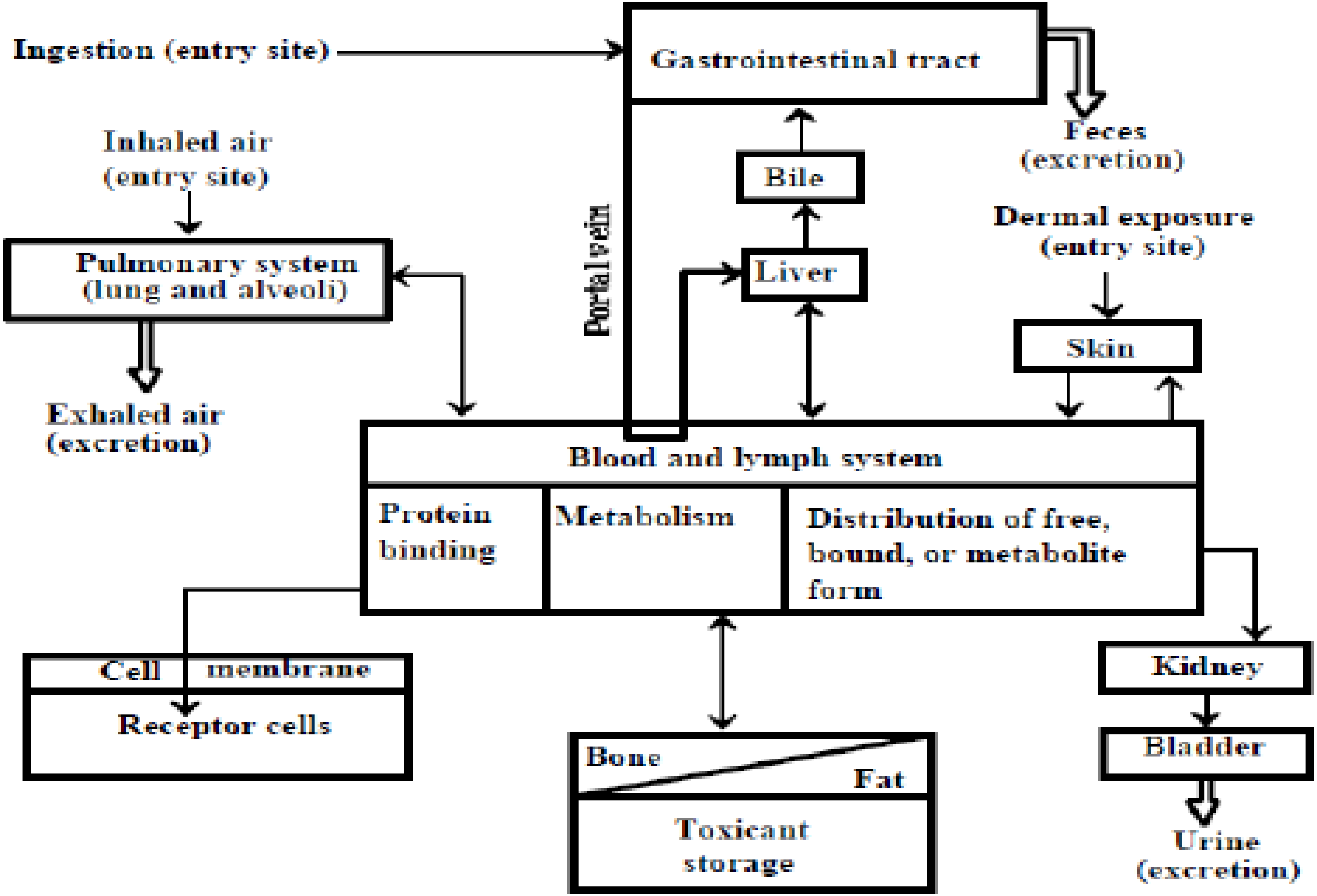


Figure 5.1 Major sites of exposure, metabolism and storage, routes of distribution and elimination of toxic substances in the bod

Cont.,

- The **defensive barriers that a toxicant may encounter vary with the route of exposure**.

- The permeability of skin is inversely proportional to the **thickness of the skin‘s stratum corneum** layer, which varies by location on the body in the following order:

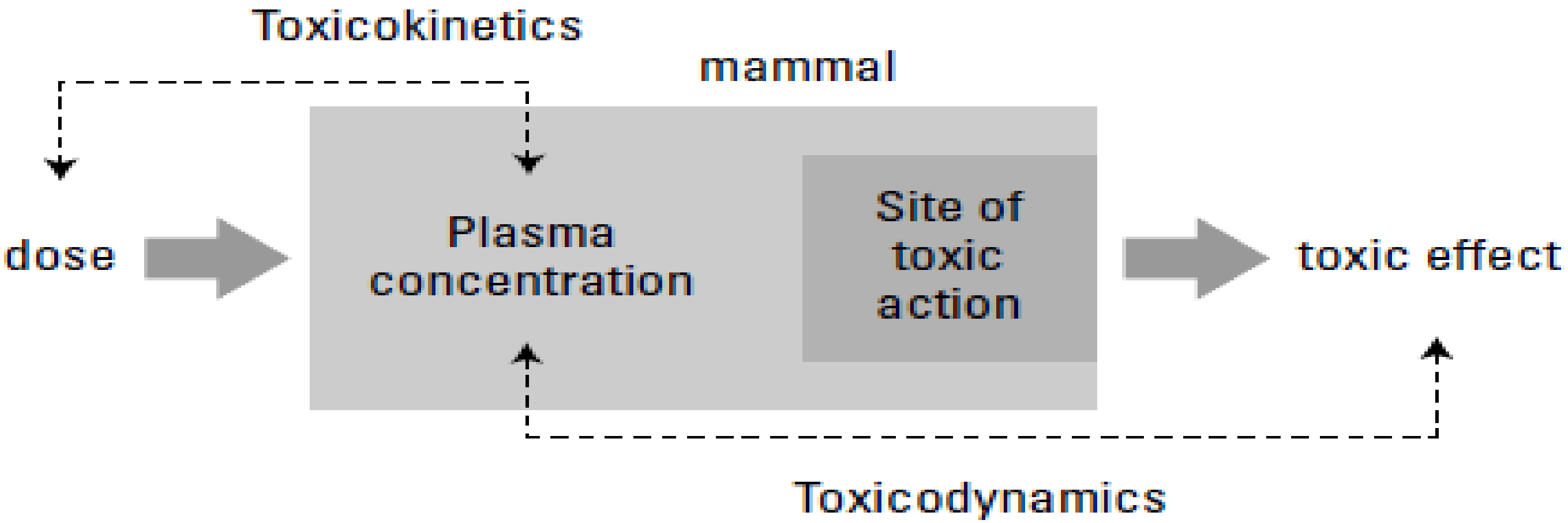
✓Soles and palms > abdomen,

✓Back, legs, arms > genital (perineal) area.

Fate

- Absorption
- Distribution
- Biotransformation (Metabolism)
- Excretion

ADME



Toxicokinetics

mammal

dose

Plasma concentration

Site of toxic action

toxic effect

Toxicodynamics

Figure 6.2. Toxicokinetics

Biological Monitoring

- Organisms can serve as indicators of various kinds of pollutants, thus serving as **biomonitors**.

❖ For example:,

✓ higher plants, fungi, lichens, and mosses can be important **biomonitors** for heavy-metal pollutants in the environment.

✓ **Fish** are important indicators and renowned symbols of ecosystem health. They are **oxygen demanding and very susceptible to chemical pollution**.

Biological Monitoring

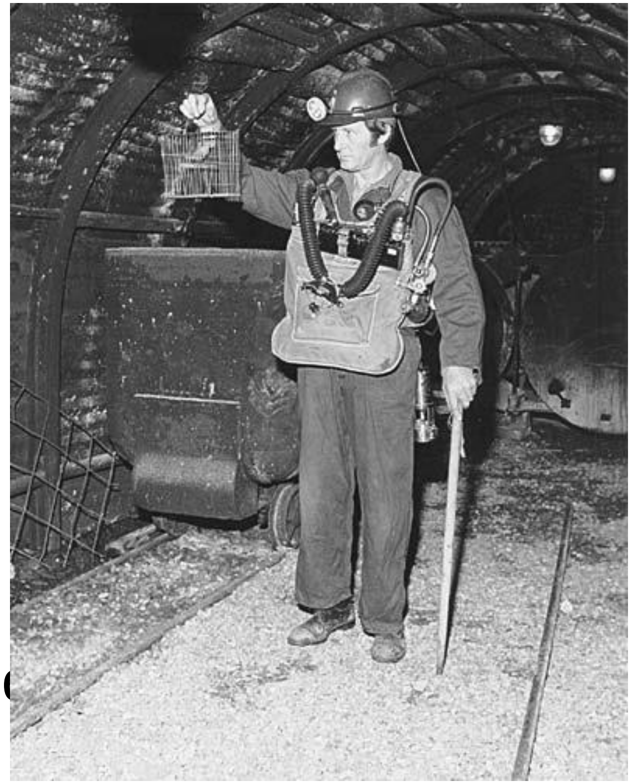
« Canary in the **coal mine** »

Human health drives

development of bioindicators

-> ecosystem services

Toxicity of : Oxygen, Metal, Canc



Cont.,

❖ **Bioindicator: qualitative**

presence/absence

❖ **Biomonitoring: quantitative effect**

Reduction diversity -> how big is the stress?

❑ **Functions of bioindicators/biomonitoring**

➢ Monitor environment

➢ Monitor ecological processes

➢ Monitor biodiversity

Cont.,

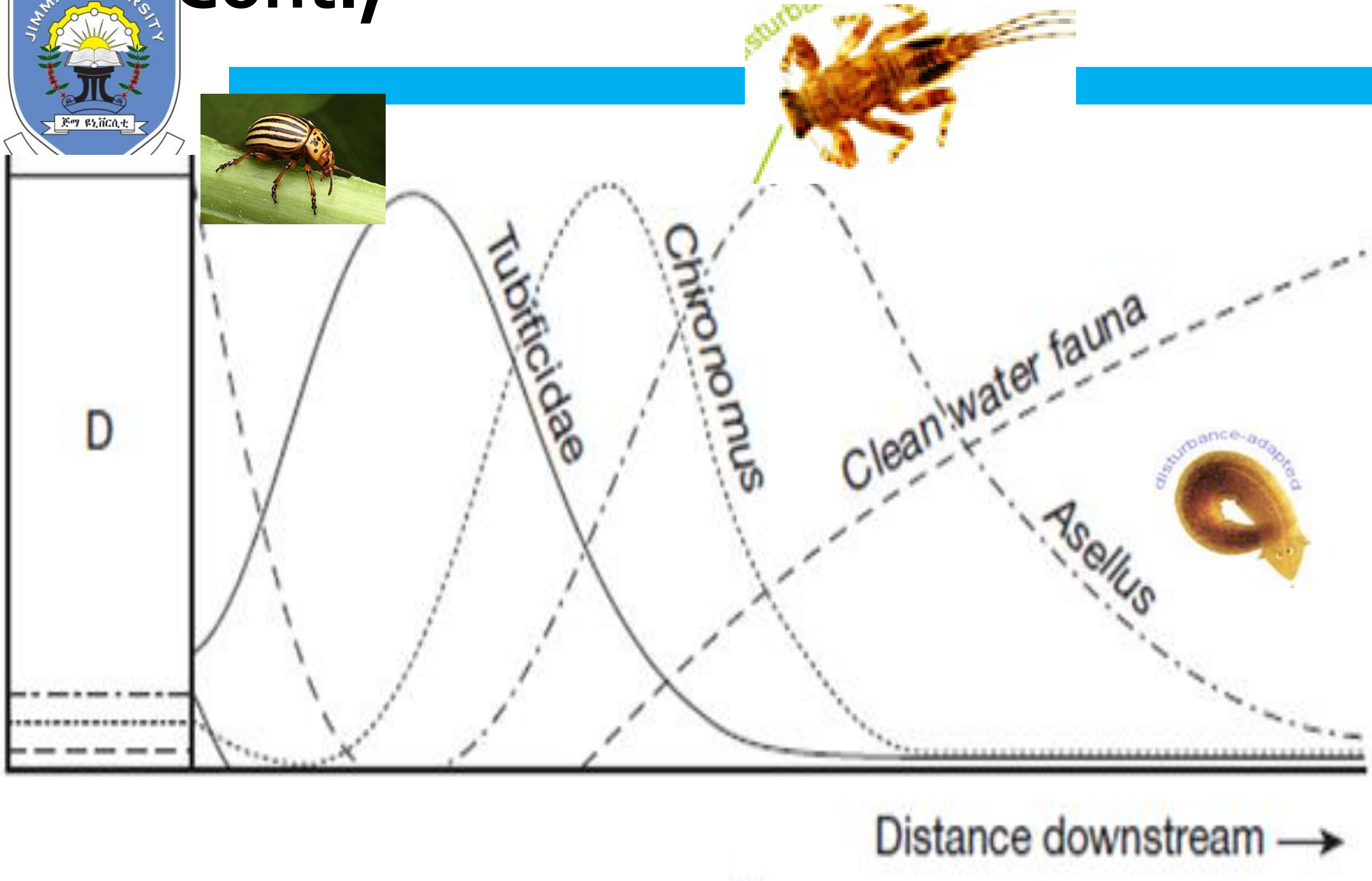
- ❑ **Biomarker**

Change in biological response related to exposure or toxic effects of chemicals

- ➢ Used for screening or monitoring

- ❑ **Bacterial indicators**
- ☐ Fecal coliform
- ☐ Escherichia coli
- ☐ Enterococci (no coliform)

Cont.,


D
Tubificidae
Chironomus
Clean water fauna
Asellus
disturbance-adapted
Distance downstream →

Biological effect

- The biological effects of **two or more toxic substances can be different in kind and degree from those of one of the substances alone**.
- Chemical interaction between substances may affect their toxicities.
- **Synergism, Potentiation, and Antagonism**

Synergism, Potentiation, and Antagonism

- When substances have the same physiologic function, their effects may be simply additive or they may be **synergistic** (the total effect is greater than the sum of the effects of each separately).
- **Potentiation** occurs when an inactive substance enhances the action of an active one, and
- **antagonism** when an active substance decreases the effect of another active one.
- Both substances may act upon the same physiologic function, or two substances may **compete for binding to the same receptor** (molecule or other entity acted upon by a toxicant).

Effects of toxicants

- **Toxicants have widely varying effects upon organisms.**
- Quantitatively, these variations include **minimum levels at which the onset of an effect is observed**, the sensitivity of the organism to small increments of toxicant, and levels at which the ultimate effect (particularly death) occurs in most exposed organisms.
- Some essential substances, such as nutrient minerals, have **optimum ranges above and below which detrimental effects are observed**.

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Dose-response relationship

- ❑ ***Dose-response relationship***, is one of the key concepts of toxicology.
- ❖ **Dose** is the amount, usually per unit body mass, of a toxicant to which an organism is exposed.
- ❖ **Response** is the effect upon an organism resulting from exposure to a toxicant.
- □ To define a dose-response relationship, it is necessary to specify a particular response, such as death of the organism, as well as the conditions under which the response is obtained, **depends on the length of time from administration of the dose.**

Cont.,

- Dose- response relationships differ among **different kinds and strains of organisms, types of tissues, and populations of cells.**
- The dose corresponding to the mid-point (inflection point) of the resulting S-shaped curve is the statistical estimate of the dose that would kill **50 % of the subjects**.
- It is designated as **LD50** and is commonly used to express toxicities.

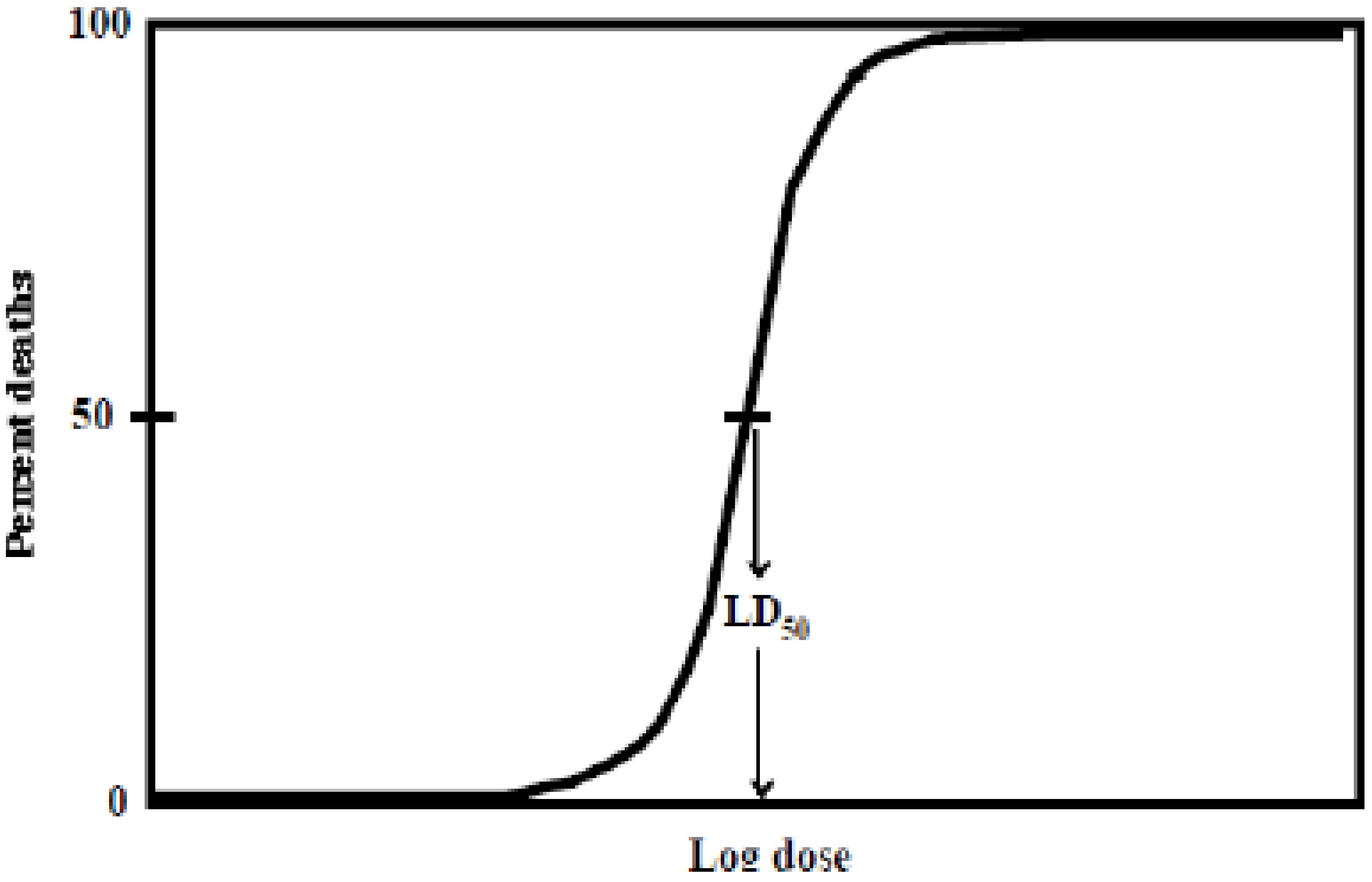

Figure 5.2 Illustration of dose – response curve in which the response is the death of the organism. The cumulative percentage of deaths of organisms is plotted on the Y axis.

Dose-response curve: LD50

Substance	LD50 for lab rat (mg/kg)	LD50 for 70 kg Human (g)
Sucrose (table sugar)	29 700	428.64
Saccahrin	14 200	204.97
Benlate (fungicide)	9 500	137.21
Vinegar	3 310	47.91
Sodium chloride (table salt)	3 000	43.37
Resmethrin (insecticide)	2 500	36.00
Malathion (insecticide)	1 375	19.84
Aspirin	1 000	14.46
Sevin (insecticide)	500	7.09
Diazinon (insecticide)	300	4.25
Caffeine	192	2.83
Gasoline	150	2.27
Nicotine	53	0.85

ii) Nonlethal and lethality Effects

- ☐ Reversible and irreversible consequence of exposure.
- ☐ In many, and perhaps most, cases, **sublethal** and **reversible** effects are of greater importance than irreversible (ultimate effect death or lethality).
- ☐ The **margin of safety** is used in connection with **drugs** to express the difference between the dose that gives a desired therapeutic effect and a harmful, potentially lethal, effect.
- ☐ This term applies to other substances, such as **pesticides,** for which it is desirable to have a large difference between the dose that kills a target species and that which harms a desirable species.

Cont.,

- Sub lethal doses of most toxic substances are eventually eliminated from an organism's system. If there is no lasting effect from the exposure, it is said to be reversible.
- In cases where the effect is permanent, it is termed irreversible. Irreversible effects of exposure remain after the toxic substance is eliminated from the organism.
- For various chemicals and different subjects, toxic effects can range from the totally reversible to the totally irreversible.

iv) Hypersensitivity and Hyposensitivity

- Some subjects are **very sensitive** to a particular poison, whereas others are **very resistant** to the same substance. These two kinds of responses illustrate **hypersensitivity and hyposensitivity, respectively.**
- Subjects in the **mid-range** of the dose-response curve are **termed normals**.
- These variations in response tend to complicate toxicology in that there is **no specific dose guaranteed to yield a particular response, even in a homogeneous population.**

Organic and Inorganic Pollutants

❑Sources Of Organic pollutants

- **Sewage** from domestic, commercial, food-processing, and **industrial sources** contains a wide variety of pollutants, including organic pollutants. Some of these pollutants, particularly oxygen demanding substances oil, grease and solids are removed by primary and secondary sewage treatment processes.
- **Soaps, detergents, and associated** chemicals are potential sources of organic pollutants.

Bio-refractory Organic Pollutants

❑ **Bio-refractory organics** are the organic compounds of most concern in waste water, particularly when they are found in sources of drinking water.

❖ These are **poorly biodegradable substances**, prominent among which are aromatic or chlorinated hydrocarbons.

➢ **The most common bio refractory organic industrial wastes** are **benzene, bornyl alcohol, bromobenzene, bromochlorobenzene**, chloroform, chloromethylethyl ether, chloronitrobenzene, chloropyridine, dibromobenzene, dichlorobenzene, ethylene dichloride, 2-ethylhexanol, isocyanic acid, methylbiphenyl, methyl chloride, nitrobenzene, styrene, tetrachloroethylene, trichloroethane, toluene.

❖ Many of these compounds have been found in drinking water, and some are known to cause taste and odor problems in water.

Naturally Occurring Chlorinated and Brominated Compounds

- Halogenated organic compounds in water are normally considered to be from anthropogenic sources.
- These are produced largely by marine species, especially some kinds of red algae, probably as chemical defense agents.
- Some marine microorganisms, worms, sponges, and tunicates are also known to produce organochlorine and organobromine compounds.

Inorganic pollutants

- Some important inorganic water pollutants are trace elements.
- Inorganic pollutant contributes to acidity, alkalinity, or salinity to water.
- **Some important inorganic pollutant species are cyanide ion, ammonia, carbon dioxide, hydrogen sulfide, nitrite, and sulfite**.

Cyanide (CN-)

- **Cyanide, a deadly poisonous substance, exists in water as HCN, a weak acid, Ka of 6x10-10.**
- The cyanide ion has a strong affinity for many metal ions, forming relatively less-toxic ferrocyanide, Fe (CN)64- , with iron (II), for example.
- **Volatile HCN is very toxic** and has been used in gas chamber executions.
- Cyanide is widely used in industry, especially for metal cleaning and electro- plating.
- Cyanide is widely used in certain mineral-processing operations.

Hydrogen sulfide (H_2S)

- **Hydrogen sulfide** is a product of the anaerobic decay of organic matter containing sulfur.
- It is also produced in the anaerobic reduction of sulfate by microorganisms and is evolved as a gaseous pollutant from geothermal waters.
- Wastes from chemical plants, paper mills, textile mills, and tanneries may also contain H2S.
- **Its presence is easily detected by its characteristic rotten-egg odor.**
- The sulfide ion has tremendous affinity for many heavy metals, and precipitation of metallic sulfides often accompanies production of H2S.

Acidity, alkalinity, and salinity

- **Aquatic biota is sensitive to extremes of pH.**
- Largely because of osmotic effects, they cannot live in a medium having a salinity to which they are not adapted.
- Thus, a freshwater fish soon succumbs in the ocean, and sea fish normally cannot live in fresh water.
- **Excess salinity soon kills plants not adapted to it**.

Cont.,

- **Industrial wastes frequently have the potential to contribute strong acid to water.**
- **Sulfuric acid produced by the air oxidation of pollutant sulfur dioxide enters natural waters as acidic rainfall.**
- In cases where the water does not have contact with a basic mineral, such as limestone, the water pH may become dangerously low.
- **Excess alkalinity and frequently accompanying high pH, generally are not introduced directly into water from anthropogenic sources.**
- However, in many geographic areas, the soil and mineral strata are alkaline and impart a high alkalinity to water.
- **Human activity can aggravate the situation-for example, by exposure of alkaline overburden from strip mining to surface water or groundwater.**

Cont.,

- **Water salinity may be increased by a number of human activities.**
- **One of the major environmental constraints on the production of shale oil, for example, is the high percentage of leachable sodium sulfate in piles of spent shale.**
- Careful control of these wastes is necessary to prevent further saline pollution of water in areas where salinity is already a problem.

Agricultural and Pharmaceutical Contaminants

- **Fertilizers: is** One of the common Agricultural contaminants.
- Crop fertilizers contain **nitrogen, phosphorus and potassium** as major components. Magnesium, sulfate and micronutrients may also be added.
- Fertilizers are designated by numbers, such as 6-12-8, showing the respective percentages of nitrogen expressed as N (in this case 6%), phosphorus as P2O5 (12%), and potassium as K2O (8%).
- Farm manure corresponds to an approximately 0.5-0.24-0.5 fertilizer.
- The organic fertilizers such as manure must undergo biodegradation to release the simple inorganic species (NO3-, HxPO4x - 3, K+) assimilable by plants.

Cont.,

- ☐ **Nitrogen fertilizers** Most modern nitrogen fertilizers are made by the Haber process, in which N2 and H2 are combined over a catalyst at temperatures of approximately 500˚C and pressures up to 1000 atm:
- ☐ The anhydrous ammonia product has a very high nitrogen content of 82%. I o the soil, for which it has a strong affinity because of its water solubility and formation of ammonium ion:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

$$NH_3(g)\ (\text{water}) \rightarrow NH_3(aq)$$

$$NH_3(aq) + H_2O \rightarrow NH_4^+ + OH^-$$

Cont.,

- It should be pointed out that ammonia vapor is toxic and NH3 is reactive with some substances.
- Improperly discarded or stored ammonia can be a hazardous waste.
- **Ammonium nitrate**, NH4NO3, is a common solid nitrogen fertilizer.
- It is made by oxidizing ammonia over a platinum catalyst, converting the nitric oxide product to nitric acid and reacting the nitric acid with ammonia.
- Ammonium nitrate contains 33.5% nitrogen. Although convenient to apply to soil, it requires considerable care during manufacture storage and use because it is explosive and toxic.
- **Urea** is another nitrogen fertilizer which is easier to manufacture and handle than ammonium nitrate.
- The overall reactio $CO_2 + 2NH_3 \rightarrow CO(NH_2)_2 + H_2O$

Cont.,

- Other compounds used as nitrogen fertilizers include:
- **Sodium nitrate, calcium nitrate, potassium nitrate, and ammonium phosphates**.
- The alkali metal nitrates tend to make soil alkaline, whereas ammonium sulfate leaves an acidic residue.

Phosphorous fertilizers

- The principal mineral is **fluorapatite**, **Ca5 (PO4)3F.**
- The phosphate from fluorapatite is relatively unavailable to plants, and fluorapatite is frequently treated with phosphoric or sulfuric acids to produce **superphosphates**:

$$2Ca_5(PO4)_3F(s) + 14H_3PO_4 + 10H_2O \rightarrow 2HF(g) + 10Ca(H_2PO_4)_2{\cdot}H_2O$$

$$2Ca_5(PO_4)_3F(s) + 7H_2SO_4 + 3H_2O \rightarrow 2HF(g) + 3Ca(H_2PO_4)2{\cdot}H_2O + 7CaSO_4$$

Cont.,

- The HF produced as a byproduct of superphosphate production can create air pollution problems.
- Phosphate minerals are rich in trace elements required for plant growth, such as boron, copper, manganese, molybdenum, and zinc.
- Ironically, these elements are lost to a large extent when the phosphate minerals are processed to make fertilizer.
- Ammonium phosphates are excellent, highly soluble phosphate fertilizers.
- Liquid ammonium polyphosphate fertilizers consisting of ammonium salts of pyrophosphate, triphosphate, and small quantities of higher polymeric phosphate anions in aqueous solution work very well as phosphate fertilizers.
- The polyphosphates are believed to have the additional advantage of chelating iron and other micronutrient metal ions, thus making the metals more available to plants.

Potassium fertilizer

- ☐ Potassium fertilizer components consist of potassium salts, generally KCl.
- ☐ Such salts are found as deposits in the ground or can be obtained from some brine.
- ☐ These salts are all quite soluble in water.
- ☐ One problem encountered with potassium fertilizers is the luxury uptake of potassium by some crops, which absorb more potassium than is really needed for their maximum growth.

Crop Protection Chemistry

- Crop Protection
  - Crop = plant → agriculture
  - Chemistry = Chemical substances

- (Chemical) substances used against unwanted organisms
  - Insects
  - Weed
  - Fungi

PPP = Securance Income of farmer

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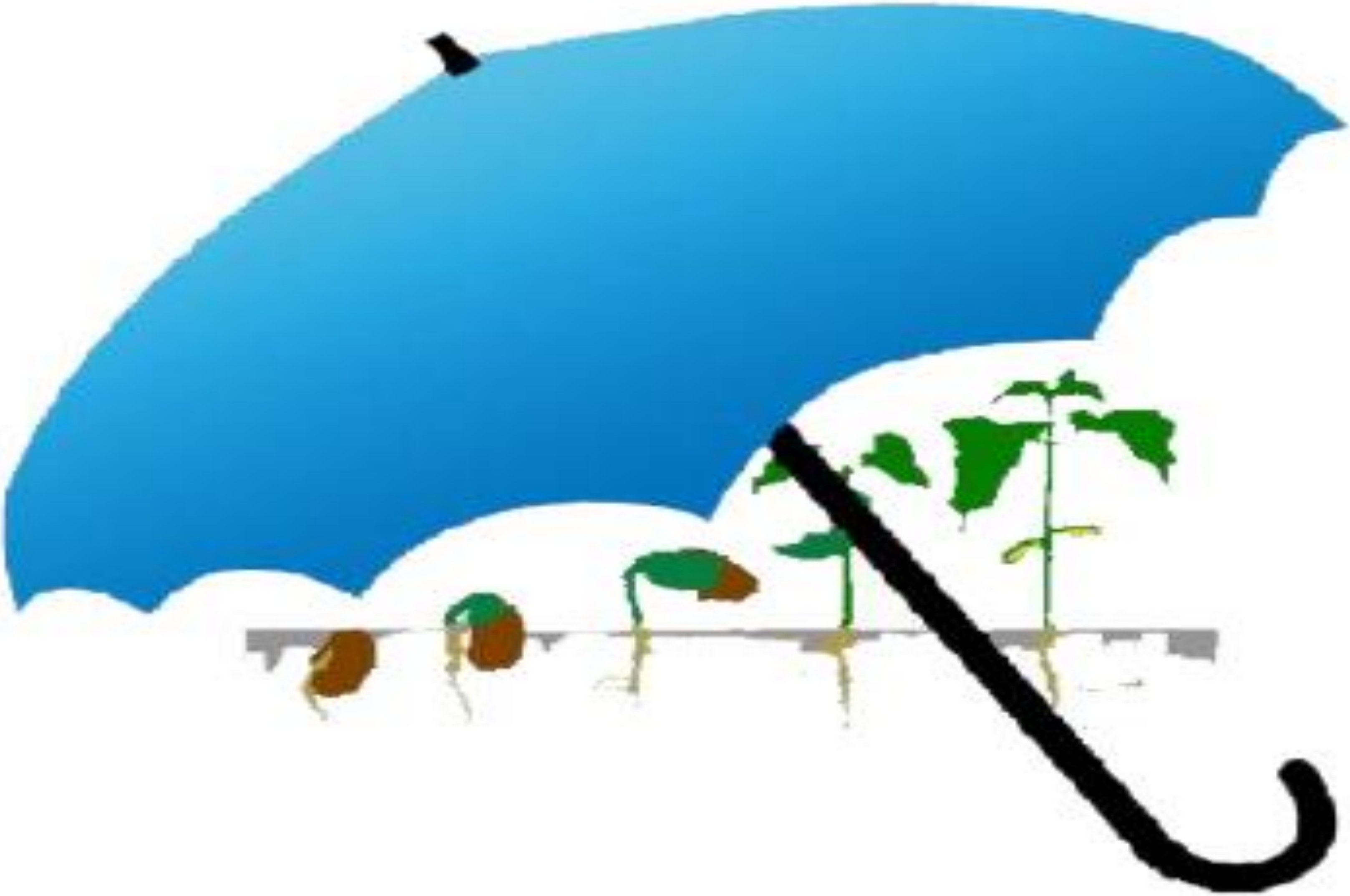

Chemical treatment

Pesticides = pest – cide

kill – pest

- **Biocides** = Living organisms – kill
- **PPP** = Plant protection products

Fungicides
Herbicides
Insecticides

SYSTEMIC PESTICIDES VS. CONTACT PESTICIDES

- ***Contact products:*** work only at the place where they are applied and are not transported via the plant sap flow
- ***Products with in depth activity*:** penetrate deeper into the leaf than contact products, but remain there and are not transported,
- ***Translaminar products*:** penetrate through the leaf and are active at the upper and lower side of the leaf,
- ***Systemic products*:** penetrate into the plant and are transported via the plant sap flow

Cont.,

Contact-Systemic

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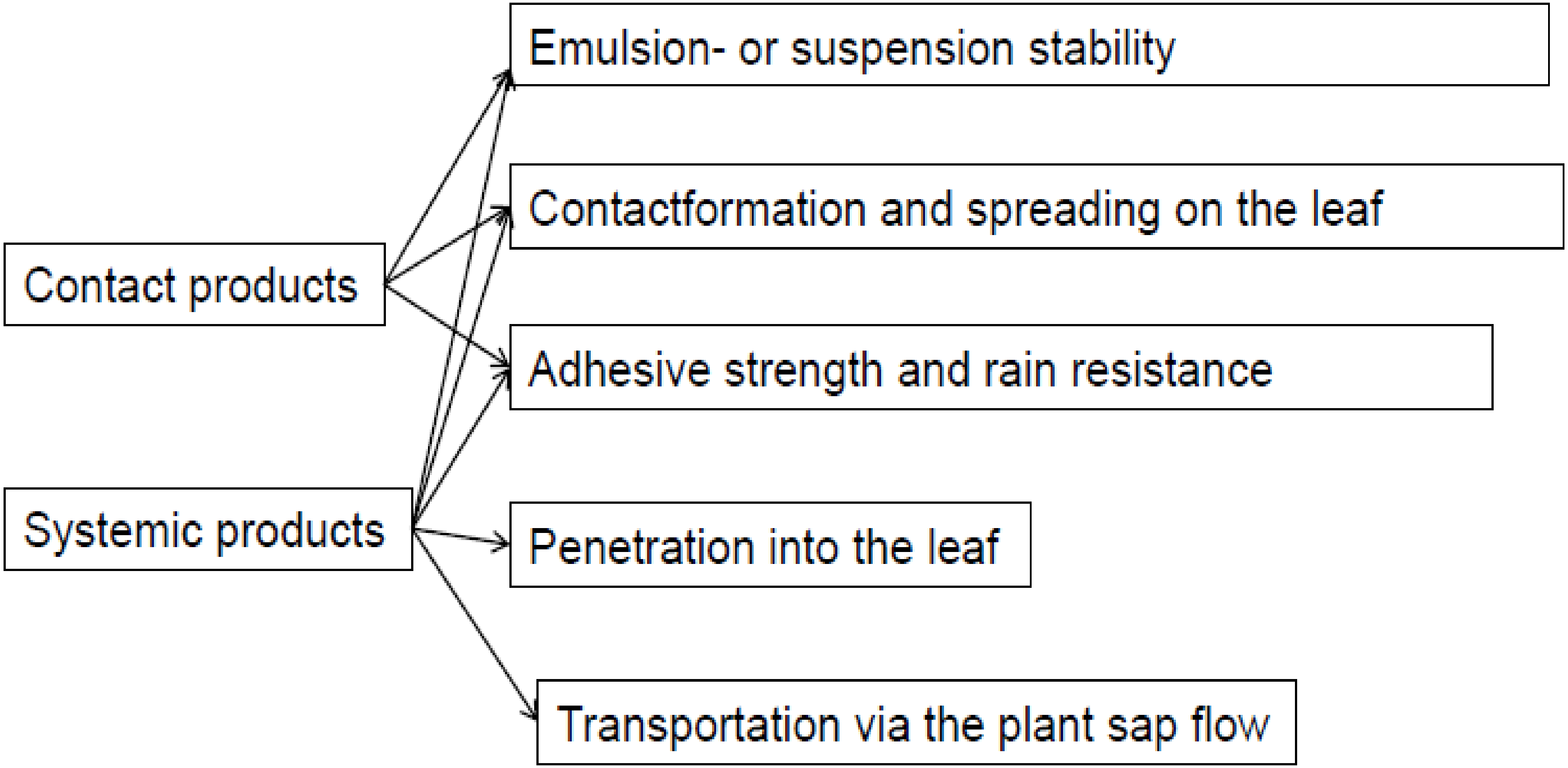


Emulsion- or suspension stability

Contactformation and spreading on the leaf

Contact products

Adhesive strength and rain resistance

Systemic products

Penetration into the leaf

Transportation via the plant sap flow

BROAD WORKING, SPECIFIC AND SELECTIVE PRODUCTS

- ***Broad working pesticides*** control a large spectrum of pests or pathogens and are also called “broadspectrum pesticides”.
- Desinfectans have, for instance, exactly the intention to make soil or instruments free of various pathogens or pests with one single treatment,
- ***Specific pesticides*** for a limited group of enemies,
- ***Selective pesticides*** spare as much as possible the natural enemies and are indispensable in integrated crop protection .


HARDI

Pesticides

- **DEFINITION (FAO, WHO 2002)**
- Any substance or mixture of substances, or micro-organisms including viruses, intended for repelling, destroying or controlling any pest, including *vectors of human or animal diseases*, *nuisance pests*, *unwanted species of plants or animals* causing harm during or otherwise interfering with the production, processing, storage, transport, or marketing of food, agricultural commodities, wood and wood products or animal feeding stuffs, or which may be administered to animals for the control of *insects, arachnids or other pests* in or on their bodies.
- The term includes substances intended for use as
- -insect or plant growth regulators
- -defoliants -dessicants
- -agents for setting, thinning or preventing the premature fall of fruit
- -substances applied to crops either before or after harvest to protect the commodity from deterioration during storage and transport.

USE

- **Agriculture – horticulture**
  - **Crop Protection**
  - **Ectoparasites on animals (ticks)**

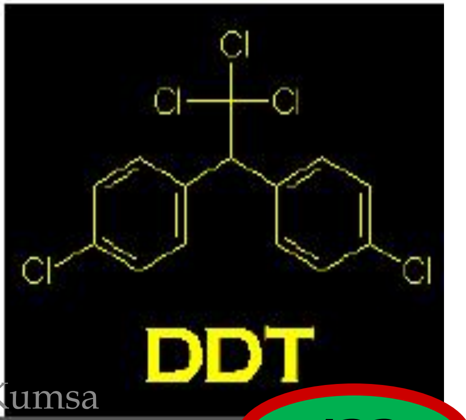
- **Industry**
  - **Protection of materials**
  - **Cooling water treatment**
  - **Post harvest**

- **Public health**
  - **Vector control (malaria,…)**
  - **General hygiene**
  - **Food quality (fungi, aflatoxins)**

- Life and working conditions
  - Traffic roads, parkings,…
  - Parks, lawns, sport and recreation, cimetaries,…
  - Hobby gardens
  - Disturbing organisms (ants, mosquitoes,…)

- Green revolution
  - Synthetic nutrients – herbicide
  - Monoculture
- DDT

Rachel Carson



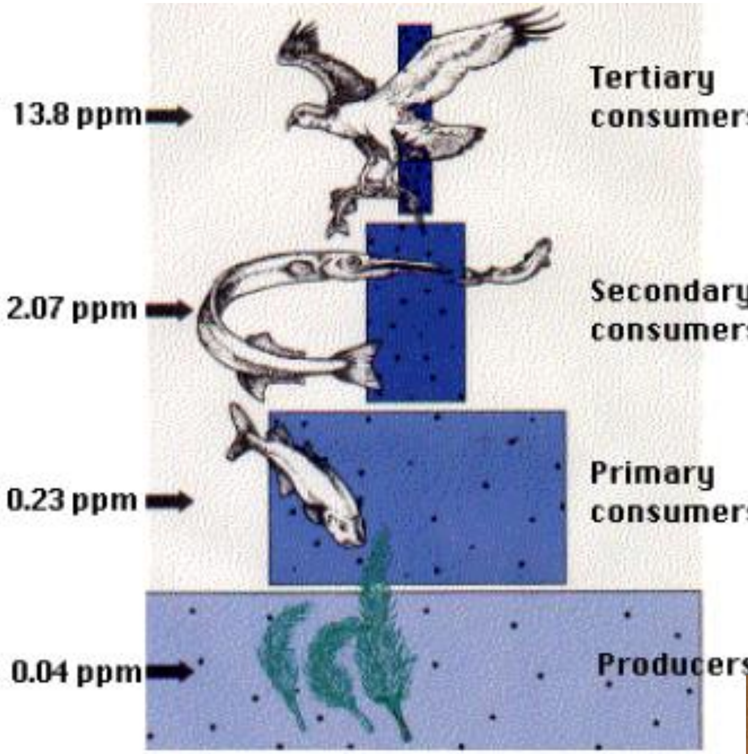
Chemical structures: DDT, DDE, DDD

DDT = C14H9Cl5 = 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane

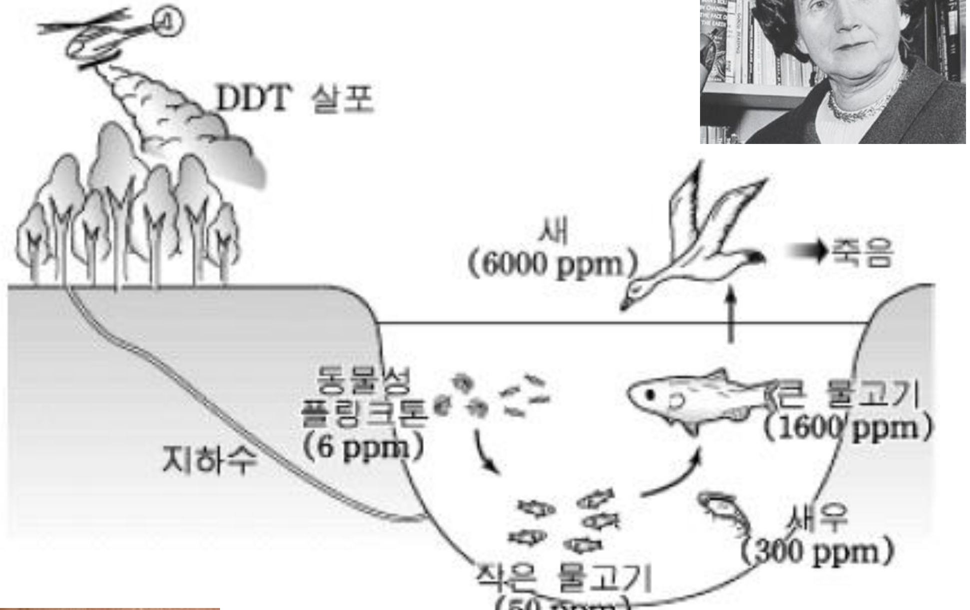
DDE = C14H8Cl4 = 1,1-dichloro-2,2-bis(chlorophenyl)ethylene

DDD = C14H10Cl4 = 1,1-dichloro-2,2-bis(p-chlorophenyl)ethane

Carson described research demonstrating that DDT caused egg shells to thin for many species of birds, increasing infant mortality rates. Effects rippled through food chain. May also affect humans directly. Difficult to prove effects on humans.



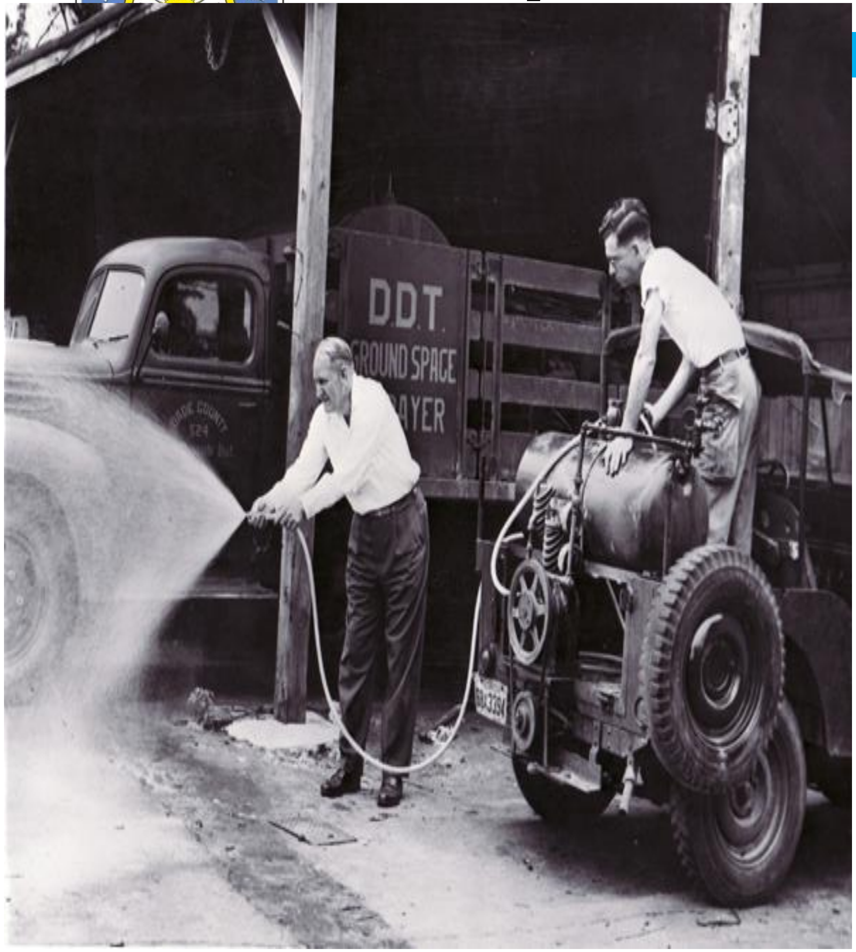
The numbers are representative values of the concentration in the tissues of DDT and its derivatives (in parts per million, ppm)



[DDT의 생물 농축 과정]

Biomagnification

Cont.,



Insecticides and related compounds

❑Use of Insecticides

- ☐ Insecticides are used for controling insects, the largest animal group. Crop protection focusses specifically on the pests:

- ➢Pests that use or damage crops grown by humans
- ➢Pests that are vectors of plant diseases
- ➢Pests that destroy harvested products
- ➢Pests that are vectors of human diseases

a nuissance for humans an

Routes of Exposure to Insecticides

- ***Stomach poisons***: insecticide must be ingested by the insect for toxic effect
- ***Contact poisons***: the insect must come into contact with insecticide for toxic effect

❖ According to the insect stage they kill, they are called ***egg-, larvae-*** *or* ***adult killing substances***.

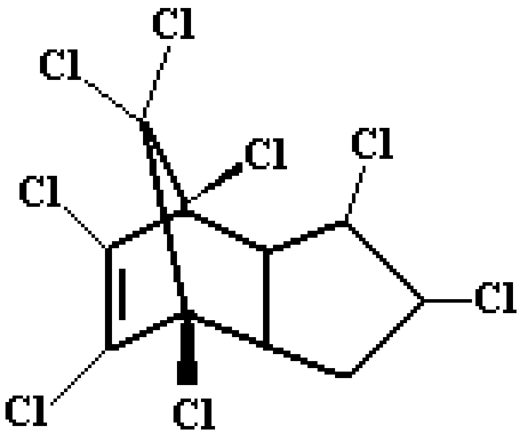
Classification

- ***Synthetic pyrethroids***
- **Malathion**
- ***Organochlor***
- ***Organofosfor***
- ***Carbamate***
- ***Other***

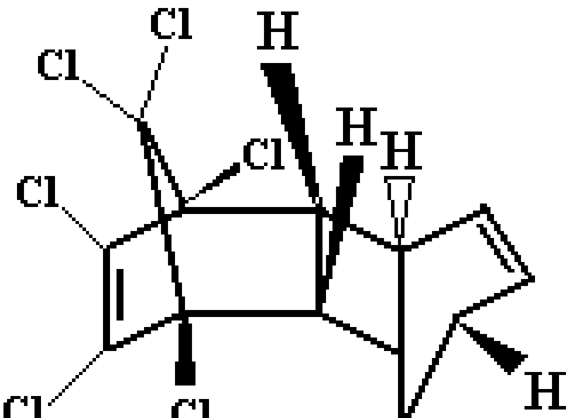
Cont.,

- **organochlor insecticides** (DDT, lindaan, aldrin, dieldrin, endosulfan,…)
- **organophosphor insecticides** (dichloorvos, malathion, parathion, chloorpyrifos,…)
- **pyrethroïds** (pyrethrine, cypermethrin, deltamethrin, cyhalothrin,…)
- **carbamates** (thiram, ziram, maneb, zineb, metam-natrium,…)

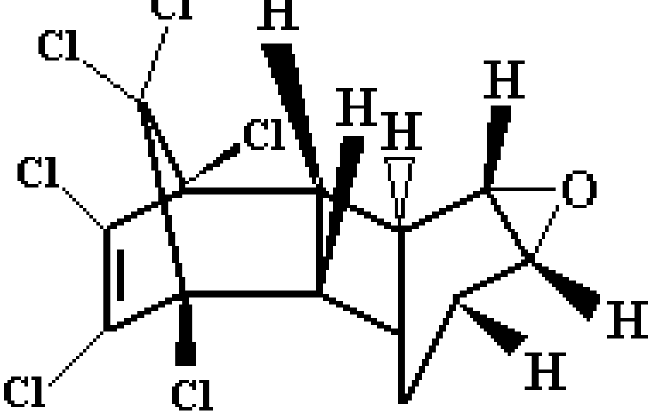
Organochlorine insecticides



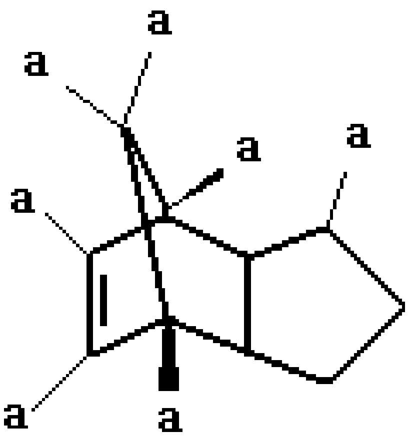
chlordane



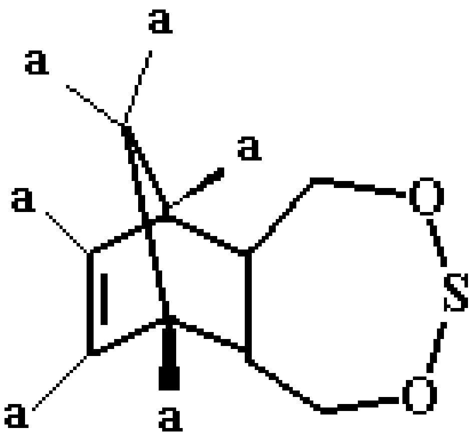
aldrin



dieldrin



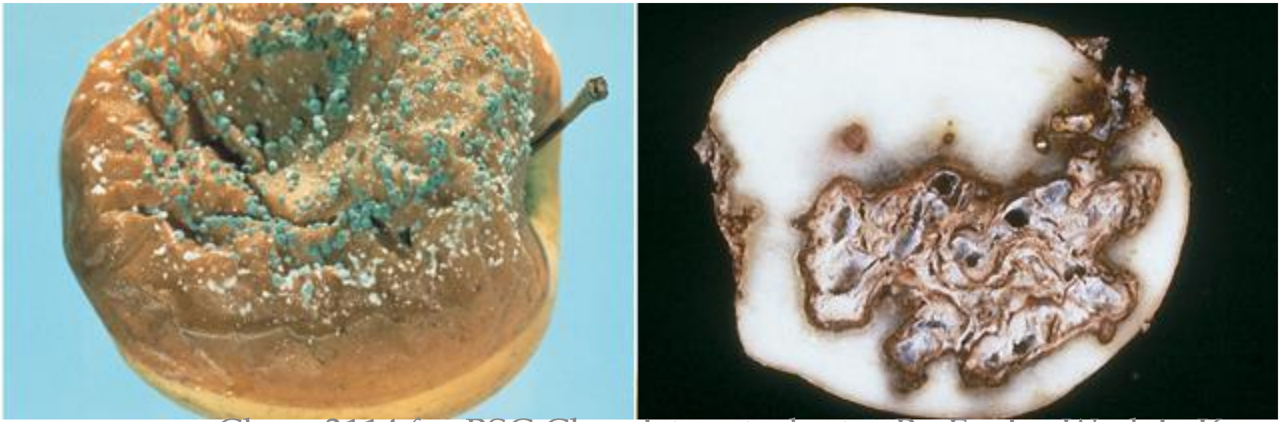
heptachlor



endosulfan

Fungicides

- Fungicides can be categorised as follows:
- ***preventive* fungicides**, protect the plant from infection by fungi: these fungicides thus have to be applied *before* infection.
- ***curative* fungicides**, can stop the development of the fungus *after* infection.
- **Protectant** fungicidal activity which results from residues on the leaf surface
- **Curative** (therapeutic) activity which results from penetration into the leaf surface



Apple and potato Fungal infection Post harvest

Herbicides

- **Herbicides** are chemicals (fytocides) against weeds. Weeds are plants that are unwanted on the place where they occur.
- **Total herbicides** are used to kill all occurring plants
- **Selective herbicides** control the weeds but spare the crops.
- The selectivity is based on properties of the product and plant species, but also on the dose, application method, application time and formulation.

- **Weeds**
- Compete with desirable plants for water, nutrients, light and space
- Contaminate crop at harvest
- Harbor pest insects, mites, vertebrates or plant disease agents
- Release toxins in the soil which may inhibit crop growth
- Example : **Glyphosate; 2,4-D(2,4-Dichlorophenoxyacetic acid)**

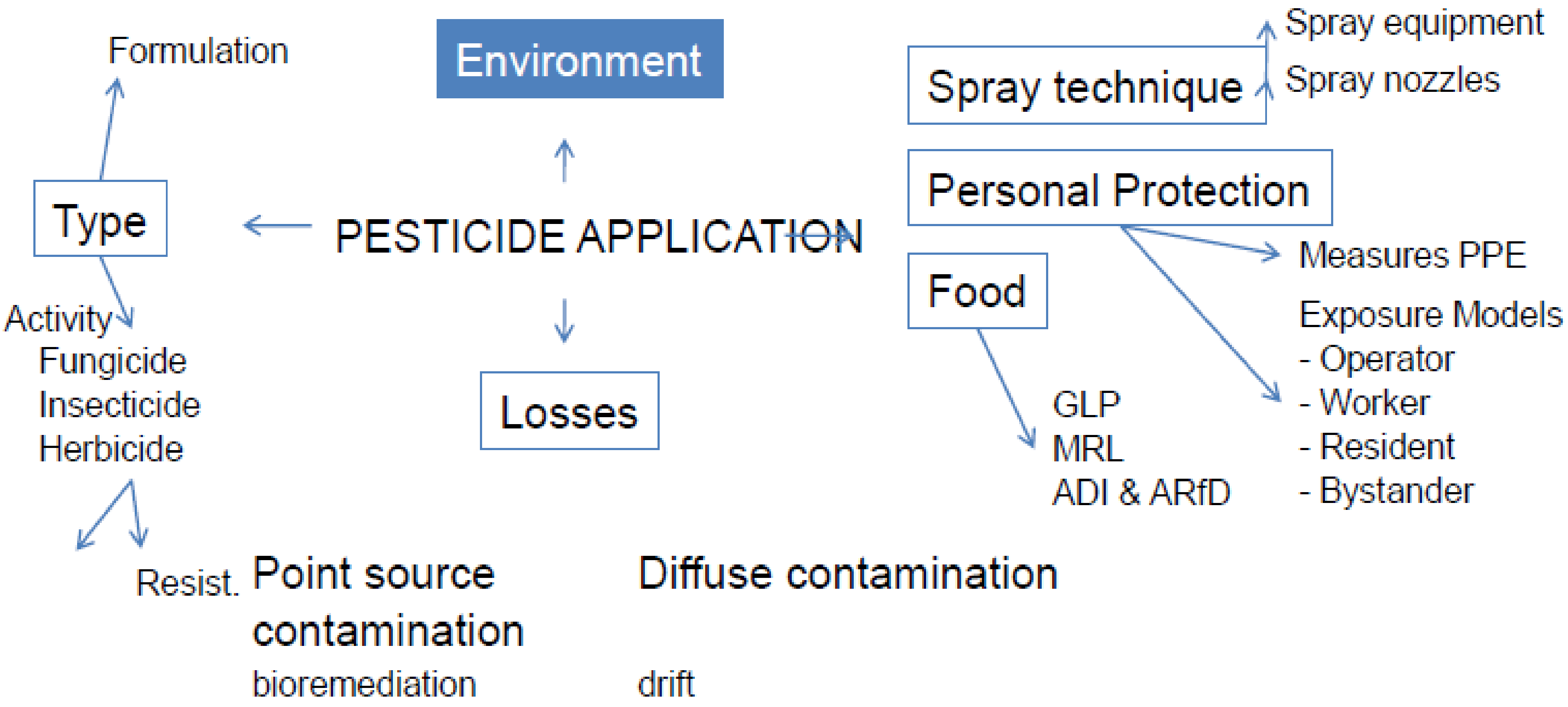
Vulnerable population groups

larger risk?

- "yopi's" = Young, Old, Pregnant, Immunodeficient

Pesticides in environment

soil	air	water	bio
sorption	fotolysis	hydrolysis	Kow
persistence	transport	solubility	
		transport	



Formulation

Environment

Spray technique

Spray equipment

Spray nozzles

Type

PESTICIDE APPLICATION

Personal Protection

Measures PPE

Exposure Models
- Operator
- Worker
- Resident
- Bystander

Food

GLP
MRL
ADI & ARfD

Activity
Fungicide
Insecticide
Herbicide

Resist.

Losses

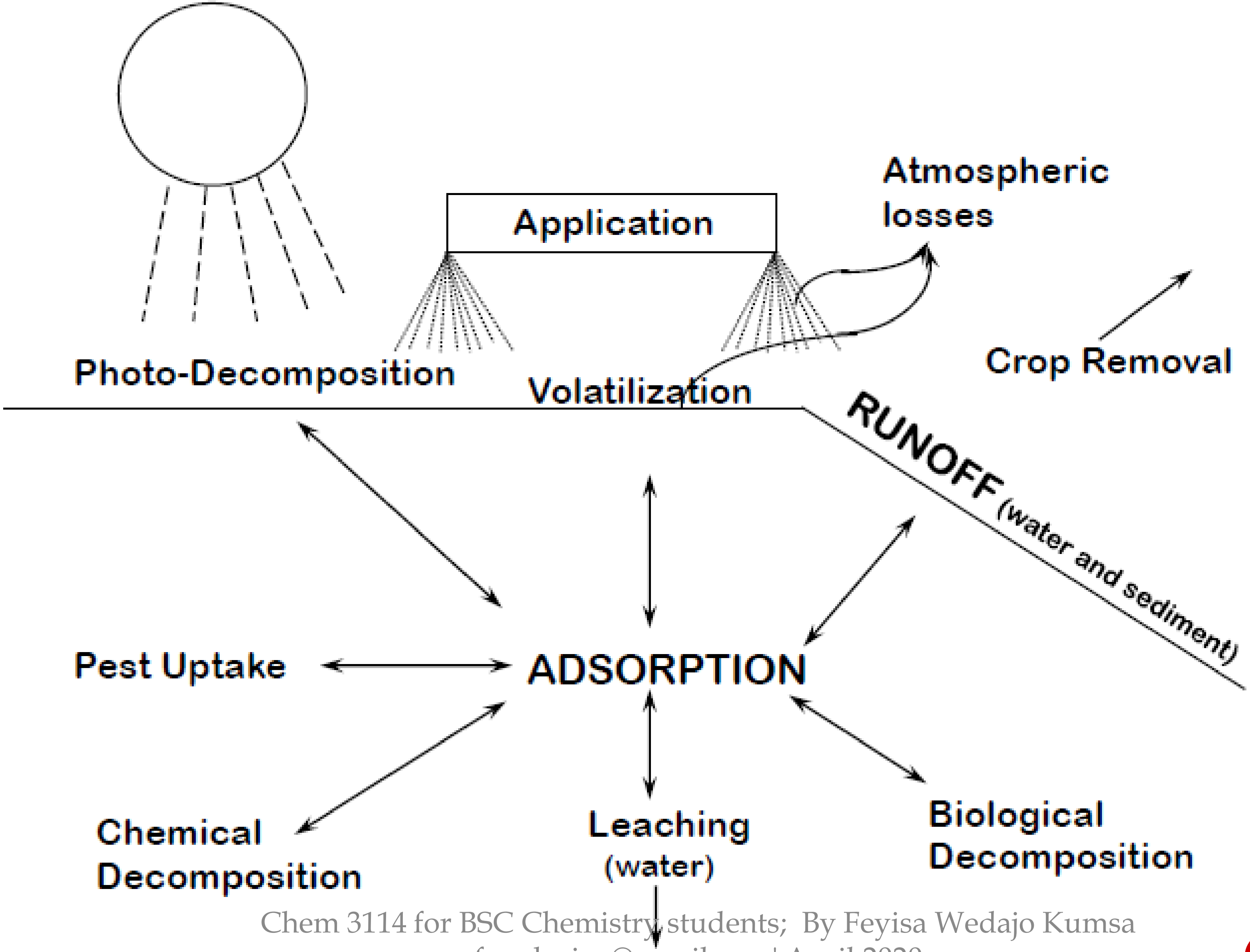
Point source contamination

bioremediation

Diffuse contamination

drift

PESTICIDE FATE IN THE ENVIRONMENT



Application

Atmospheric losses

Photo-Decomposition

Volatilization

Crop Removal

RUNOFF (water and sediment)

Pest Uptake

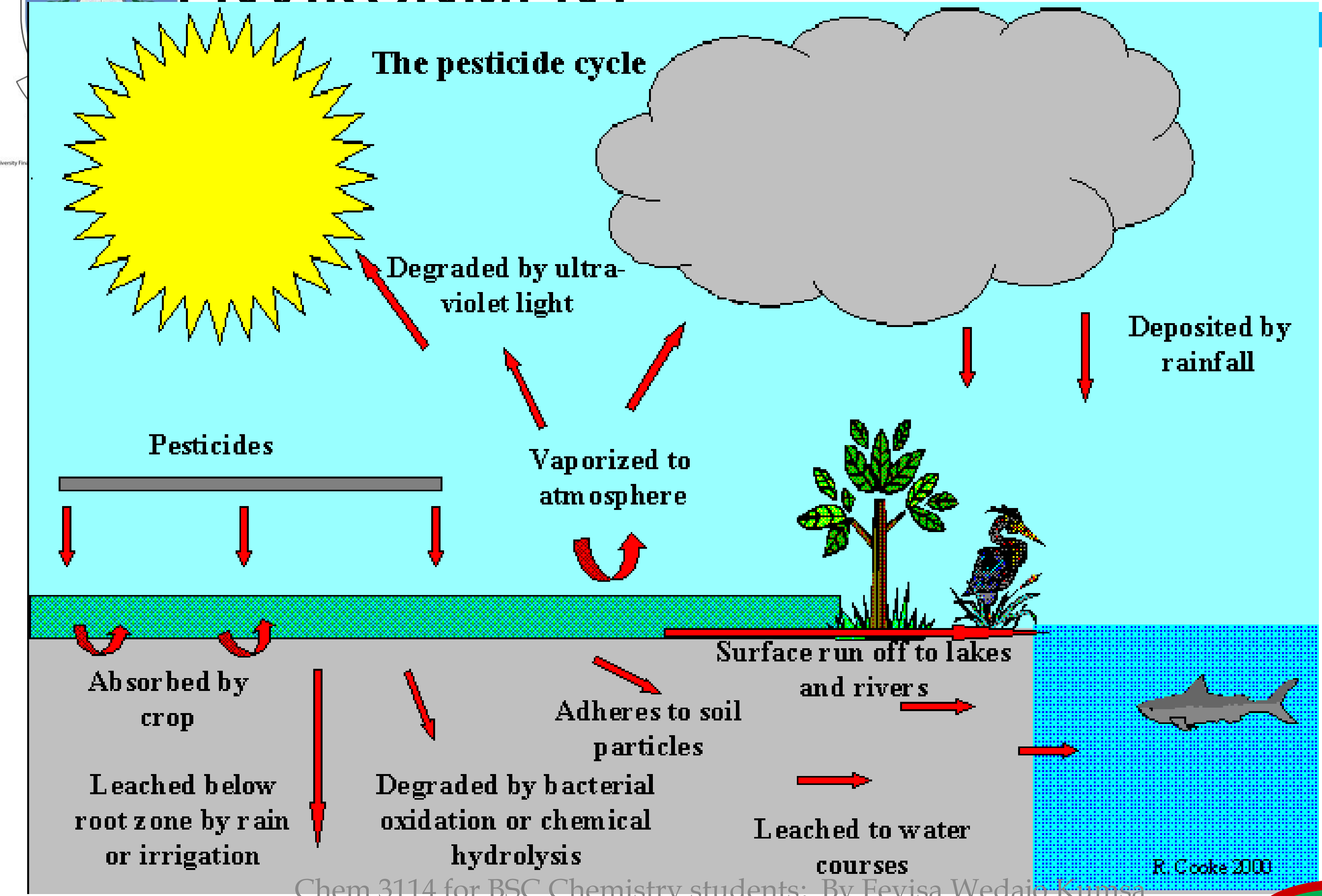
ADSORPTION

Chemical Decomposition

Leaching (water)

Biological Decomposition

PESTICIDE FATE IN THE ENVIRONMENT



Effect of pesticides

- After application in a field, pesticides are subjected to three main types of processes:
  - **Adsorption** - pesticides can become attached to particles of soil or organic matter
  - **Transfer** - they can be moved from the point to which they were applied
  - **Degradation** - they can be broken down into less complex compounds.

- The extent to which each of these processes act upon a pesticide varies depending on: **the properties of the pesticide, the soil, the weather and the crop**

Cont.,

❑Transfer

❑Pesticides can be moved from the point to which they were applied in a variety of ways:

- **volatilization** (evaporation)
- **runoff -** movement in water across the surface of land
- **leaching -** movement through the soil towards groundwater
- **plant uptake-** Pesticides are applied either to the soil or to the foliage. In either case, some pesticide is likely to taken into the plant through either the roots or leaves

Cont.,

- **Runoff** is the movement of water over the soil surface when rain falls faster than it can be absorbed by the soil.
- **The amount of runoff depends on many factors:**
  - **Type of soil (greater on clay than on sand**)
  - **Slope of the land** (the steeper the slope, the greater the potential for runoff)
  - **Condition of the soil surface** (more runoff from bare soil than from fields covered with living crops or crop residues)
  - **The amount and intensity** of rainfall following application
  - **Moisture content of the soil** (the wetter the soil to begin with, the less rain it can absorb)
  - **Length of time after application before rain** (the greater the time between application and rainfall, the less pesticide there will be in the runoff)

Leaching

- **Leaching** refers to the movement of materials down through the soil with water.
- The risk of a product being leached depends on its solubility in water, its tendency to be bound to soil particles and its persistence.
- To be leached, a pesticide must first be dissolved in the soil water. The longer the pesticide remains in its active form in the soil water, the greater the risk of it leaching into the groundwater.

Plant uptake

- Pesticides are applied either to the soil or to the foliage.
- In either case, some pesticide is likely to taken into the plant through either the roots or leaves.
- Pesticide taken up by plants is protected against runoff or leaching.
- Once within crop plants, pesticides are degraded through chemical reactions.

Degradation

- With the possible exception of pesticides that have leached into the groundwater, all pesticides are eventually degraded into harmless components in a variety of ways:

- **Microbial breakdown:** the pesticide is broken down by fungi, bacteria or other micro-organisms living in the soil, on the surface of plants or in surface water.
- **Chemical degradation:** the pesticide reacts with other compounds in the soil, especially water, to form non-toxic compounds.
- **Photo-decomposition:** some pesticides are broken down by sunlight.

Pharmaceutical Contaminants

❖**Pharmaceutical agents** are greatly increasing in numbers and kinds, with greater likelihood of releases into the environment.

❖Certain pharmaceuticals are now attracting attention as a potentially new class of water pollutants.

□ **Such drugs are:** antibiotics, anti-depressants, anti-cancer drugs, pain killers, cholesterol-lowering agents, steroids, caffeine and reproductive hormones have been detected in various water sources.

□ The presence of pharmaceuticals in our water ways and drinking water **has gained national attention among lawmakers, regulators, and the public.**

Cont.,

- **Pharmaceutical Contaminants come from different sources.**
- **The main ones are:** Pharmaceutical industries, hospitals and other medical facilities are obvious sources, but households also contribute a significant share.
- People often **dispose of unused medicines by flushing** them down toilets, and human excreta can contain varied incompletely metabolized medicines.
- These drugs can pass intact through conventional sewage treatment facilities, into waterways, lakes and even aquifers.
- Further, discarded pharmaceuticals often **end up at dumps and landfills, posing** a threat to underlying groundwater.

Nitrogen and phosphorous Compounds

- Do you Mention some of the common nitrogen and phosphorous compounds and also Describe their sources?
- Explain the effect of nitrogen and phosphorous compounds the environment?

Cont.,

- A number of plants are relatively susceptible to NO_2. Nitric acid is an important constituent of precipitation.
- Together with H_2SO_4 it causes **acid rain**, which negatively affects crops and soils.
- At **increasing nitrogen concentrations** in surface layers, plankton production increases, leading to algal blooms. This may occur in any type of surface water.
- Large amounts of **nitrate may cause eutrophication, which means an excess of nutrients** resulting in oxygen deprivation and fish deaths.

Phosphorus and its compounds

- ☐ Phosphorus is a key element in all known forms of life.
- ☐ Inorganic phosphorus in the form of the phosphate PO43– plays a major role in biological molecules such as DNA and RNA where it forms part of the structural framework of these molecules.
- ☐ Living cells also use phosphate to transport cellular energy in the form of adenosine triphosphate (ATP).
- ☐ ATP is also important for phosphorylation, a key regulatory event in cells.
- ☐ Phospholipids are the main structural components of all cellular membranes.
- ☐ Calcium phosphate salts assist in stiffening bones.

Toxic nature of Phosphorus and its compounds

- Organic compounds of phosphorus form a wide class of materials, some of which are extremely toxic.
- **Fluorophosphate** esters are among the most potent neurotoxins known.
- A wide range of organophosphorus compounds are used for their toxicity to certain organisms as **pesticides** (herbicides, insecticides, fungicides, etc.) and weaponised as nerve agents.
- Most inorganic phosphates are relatively nontoxic and essential nutrients.
- Some of environmentally adverse effects of phosphates are **eutrophication** and algal blooms in surface waters and lakes.

Toxic Heavy Metals and Organo-Metallic Compounds

- Organometallic compounds, contain metals bound to organic entities by way of a carbon atom and do not dissociate reversibly at lower pH or greater dilution.
- have at least one bond between the metal and a C atom on an organic group, as well as other covalent or ionic bonds between the metal and atoms other than carbon.
- Because they have at least one metal-carbon bond
- **Examples are** monomethylmercury chloride, CH3HgCl, phenyldichloroarsine, C6H5AsCl2

Toxicity of Organometallic Compounds

- ☐ Organometallic compounds have a variety of toxic effects.
- ☐ They often behave in the body in ways totally unlike the inorganic forms of the metals,
- ☐ due to the fact that compared with inorganic forms; organometallic compounds have an organic nature, higher lipid solubility, and greater ability to penetrate cell membranes.
- ☐ **Examples:**
- ➢ **lead**, Pb (C2H5)4, a colorless, oily liquid that was widely used as a gasoline additive to boost octane rating.
- ➢ **Methylated mercury species,** CH3Hg+ and (CH3)2Hg, are produced by anaerobic bacteria. They are extremely toxic.
- ➢ **Nickel tetra carbonyl** (Ni (CO)4), cobalt carbonyl, and iron pentacarbonyl.

Toxic Heavy metals

- Some of them are dangerous to health or to the environment **(e.g. mercury, cadmium, lead, chromium),** some may cause corrosion (**e.g. zinc, lead)**, some are harmful in other ways (e.g. **arsenic** may pollute catalysts).
- The main problems associated with the persistence of heavy metals is the potential for **bioaccumulation and biomagnification** causing heavier exposure for some organisms than is present in the environment alone.

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Mercury

- Mercury is found in batteries, thermometers and barometers.
- It can also be found in fungicides used in the agricultural industry.
- **In medicine, mercury is used in dental amalgams and various antiseptic substances.**
- It can also be found in deep sea water fish. Mercury is toxic in any form.
- Mercury poisoning can result from vapor inhalation, ingestion, injection, or absorption through the skin.

Cont.,

- **Nervous, digestive and renal systems are most commonly affected in mercury exposure.**
- Long-term effects on the nervous system are most worrying.
- Children and pregnant women are especially vulnerable to mercury exposure.
- **i) Elemental mercury** in its pure liquid form elemental mercury,
- **ii) Inorganic mercury**
- **iii) Organic mercury**

Reported toxicity of mercury

- Minamata Bay area of Japan during the period 1953–1960.
- A total of 111 cases of mercury poisoning and 62 deaths were reported among people who had consumed seafood from the bay that had been contaminated with mercury waste from a chemical plant that drained into Minamata Bay.
- The level of metal in the contaminated seafood was 5–20 parts per million.
- toxicological effects of mercury are:
  - Neurological damage, including irritability, paralysis, blindness, or insanity; chromosome breakage; and birth defects.
  - The milder symptoms of mercury poisoning such as depression and irritability have a psychopathological character.

Mercury Poisoning

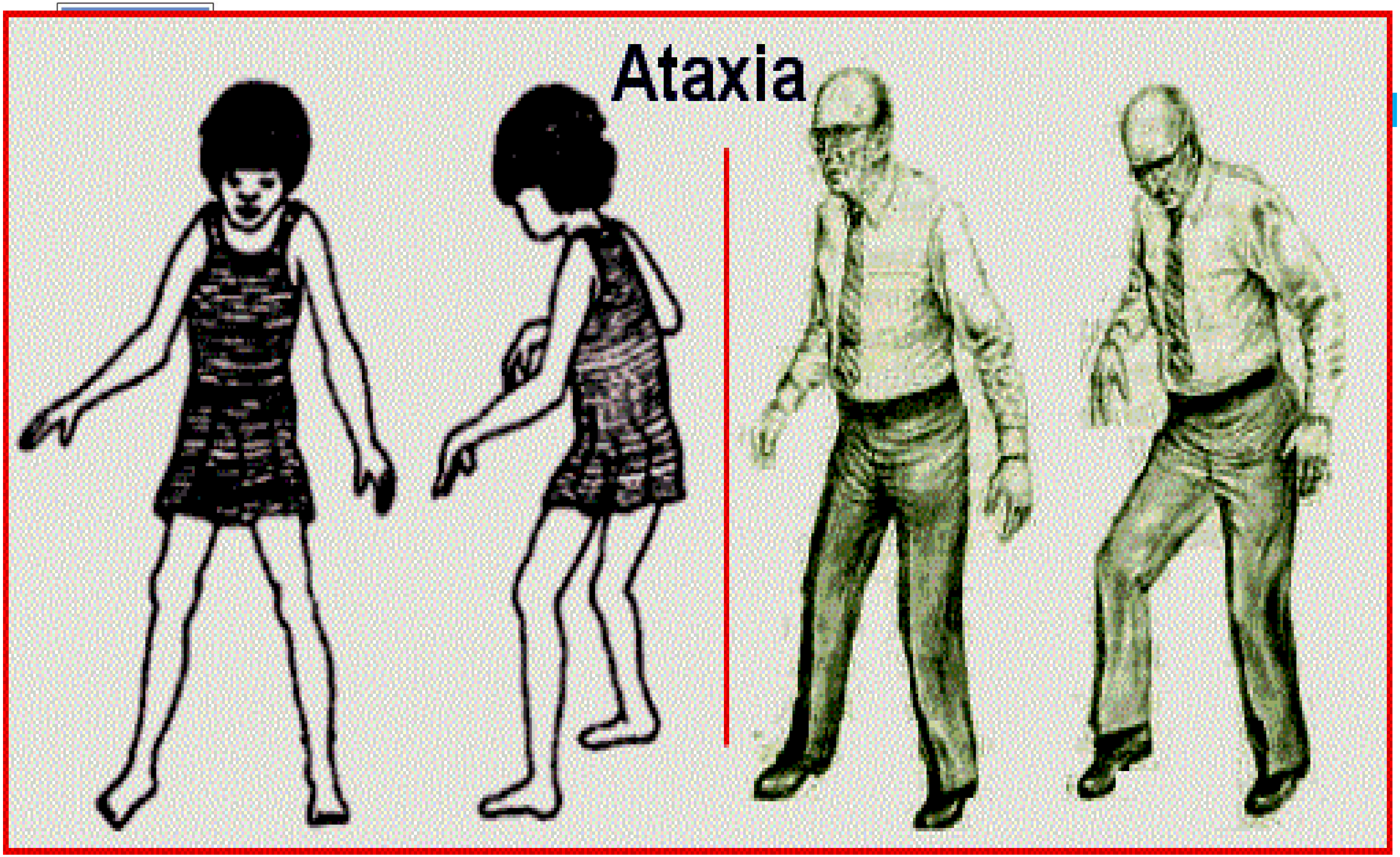
Exposure : High toxicity: **mercurialis**

Minamata Disease

- -Ataxia
- -Impairment of speech & hearing

Acrodynia **('Pink Disease')**

- -Pain
- -Pink discolouration


Ataxia

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Lead

- Inorganic **lead** arising from a number of industrial and mining sources occurs in water in the +2 oxidation state.
- In addition to pollutant sources, lead-bearing limestone and galena (PbS) contribute lead to natural waters in some locations.
- Acute lead poisoning in humans may cause severe dysfunction of the **kidney, reproductive system, liver, brain, and central nervous system leading to sickness or death.**
- Lead poisoning from environmental exposure is thought to have caused mental retardation in many children.
- Mild lead poisoning causes anemia. The victim may have headaches and sore muscles, and may feel generally fatigued and irritable.

Arsenic

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- Inorganic and organic **arsenic** occur naturally in the environment, with inorganic forms being most abundant.
- Inorganic arsenic is associated with other metals in igneous and sedimentary rocks, and it also occurs in combination with many other elements, especially oxygen, chlorine, and sulfur.
- Organic arsenic contains carbon and hydrogen. Both inorganic and organic forms exist naturally in soils, plants, animals, and humans.
- Water-soluble arsenites (the trivalent form, As III) and arsenates (the pentavalent form, As V) are the most common forms.

Arsenic Toxicity

- Arsenic has been recognized as a poison since ancient times.
- In past centuries it was used to treat syphilis, and decades ago it was a common active ingredient in pesticides and was also a common wood preservative.
- Today, about 90% of arsenic produced is used as a wood preservative (chromated copper arsenate).
- Although organic arsenicals continue to be used as pesticides, primarily on cotton, inorganic compounds can no longer be used.
- the U.S. Environmental Protection Agency (EPA) has classified inorganic arsenic as a known human carcinogen

arsenic poisoning in Bangladesh/India

- arsenic
  - Epidemiology →
    - Dermal disease
    - Cardiovascular disease
    - Skin cancer
    - Bladder cancer
    - Diabetes mellitus
  - Cytotoxicity →
    - Cell cycle arrest, autophagy
    - Cell aberrant differentiation
    - Cell dysfunction, apoptosis
    - Cell excess proliferation
  - Genotoxicity →
    - Deletion mutations
    - Oxidative DNA damage
    - DNA strand breaks
    - Sister chromatid exchanges
    - Chromosomal aberrations

Skin cancer (below) on the palm of a patient who ingested arsenic over a prolonged period of time from a contaminated well (photo courtesy the Arsenic Foundation).

Chromium

- **Chromium** is of crucial importance because of its use in stainless steel and super alloys.
- These materials are vitally important to industrialized societies because of their applications in jet engines, nuclear power plants, chemical-resistant valves, and other applications in which a material that resists heat and chemical attack.
- Chromium (VI) (chromate) is a toxic form of the metal and its uses should be eliminated wherever possible.
- The use of chromium in leather tanning and miscellaneous chemical applications should be curtailed.

Health Effects of Hexavalent Chromium

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- Hexavalent chromium is a toxic form of the element chromium. Hexavalent chromium compounds are man-made and widely used in many different industries.
- Some major industrial sources of hexavalent chromium are:
- chromate pigments in dyes, paints, inks, and plastics
- chromates added as anti-corrosive agents to paints, primers and other surface coatings
- chrome plating by depositing chromium metal onto an item‘s surface using a solution of chromic acid
- particles released during smelting of ferrochromium ore
- fume from welding stainless steel or nonferrous chromium alloys
- impurity present in Portland cement

Summery

- **Toxicity** is of the utmost concern in dealing with hazardous substances. **Toxicology** is the science of poisons.
- **A poison, or toxicant**, is a substance that is harmful to living organisms because of its detrimental effects on tissues, organs, or biological processes.
- **Acute local exposure** occurs at a specific location over a time period of a few seconds to a few hours and may affect the exposure site, particularly the skin, eyes, or mucous membranes.
- **Chronic systemic exposure** differs in that the exposure occurs over a prolonged time period.

Cont.,

- **Biomonitors** are organisms that can serve as indicators of various kinds of pollutants.
- **Additive** effect of pollutants is substances that have the same physiologic function.
- **Synergistic effect** is the total effect is greater than the sum of the effects of each separately.
- **Potentiation** occurs when an inactive substance enhances the action of an active one.
- **Antagonism is** the effect when an active substance decreases of another active one.
- **Dose** is the amount, usually per unit body mass, of a toxicant to which an organism is exposed.
- **Response** is the effect upon an organism resulting from exposure to a toxicant.

Cont.,

- **Organic pollutants** are sewage from domestic, commercial, food-processing, and industrial sources contains a wide variety of pollutants, including organic pollutants.
- **Inorganic** pollutants are trace elements and contribute to acidity, alkalinity, or salinity to water.
- Other important inorganic pollutant species are cyanide ion, CN-, is probably the most important. Others include ammonia, carbon dioxide, hydrogen sulfide, nitrite, and sulfite.

Cont.,

- **Pesticides** are Chemicals used in the control of invertebrates include **insecticides**, **molluscicides** for the control of snails and slugs, and **nematicides** for the control of microscopic roundworms.
- **Polychlorinated biphenyls (PCB's)** are benzene ring containing compounds that have very high chemical, thermal, and biological stability; low vapor pressure; and high dielectric constants.
- **Chlorofluorocarbons** (**CFC**s), such as dichlorodifluoromethane, commonly called **Freons**, are volatile 1- and 2-carbon compounds that contain Cl and F bonded to carbon.

Cont.,

- Toxic metals are elements that can cause detrimental effect on the environment
- **Organo-Metallic Compounds** are organic compounds that interact with trace metals or organometallic compounds are those in which metals are bound to carbon atoms in hydrocarbon groups or, in the case of carbonyls, to CO molecules.

Exposure assessment

- Humans may be exposed to a variety of substances from multiple exposure routes

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- Exposure assessment endeavors to answer:
  - Who or what is exposed?
  - How does exposure occur?
  - How much exposure occurs?
  - How often, and for how long, does exposure occur, i.e. what is its frequency and duration ?

Cont.,

- Humans are exposed through:
  - Environment (**Environmental exposure**)
  - Products (**Consumer exposure**)
  - Workplace (**Occupational exposure**)

- Humans are exposed via:
  - **Oral route**
  - **Inhalation route**
  - **Dermal route**
  - **Directly or indirectly** (e.g. soil ingestion vs. food)

Human risk assessment (HRA)

- is the *process* of quantifying the probability of an adverse effect to human individuals exposed to chemicals
- It determines the harmful effects and the relation with exposure
- It characterises the risk in order to be able to manage it
- It starts from **data**

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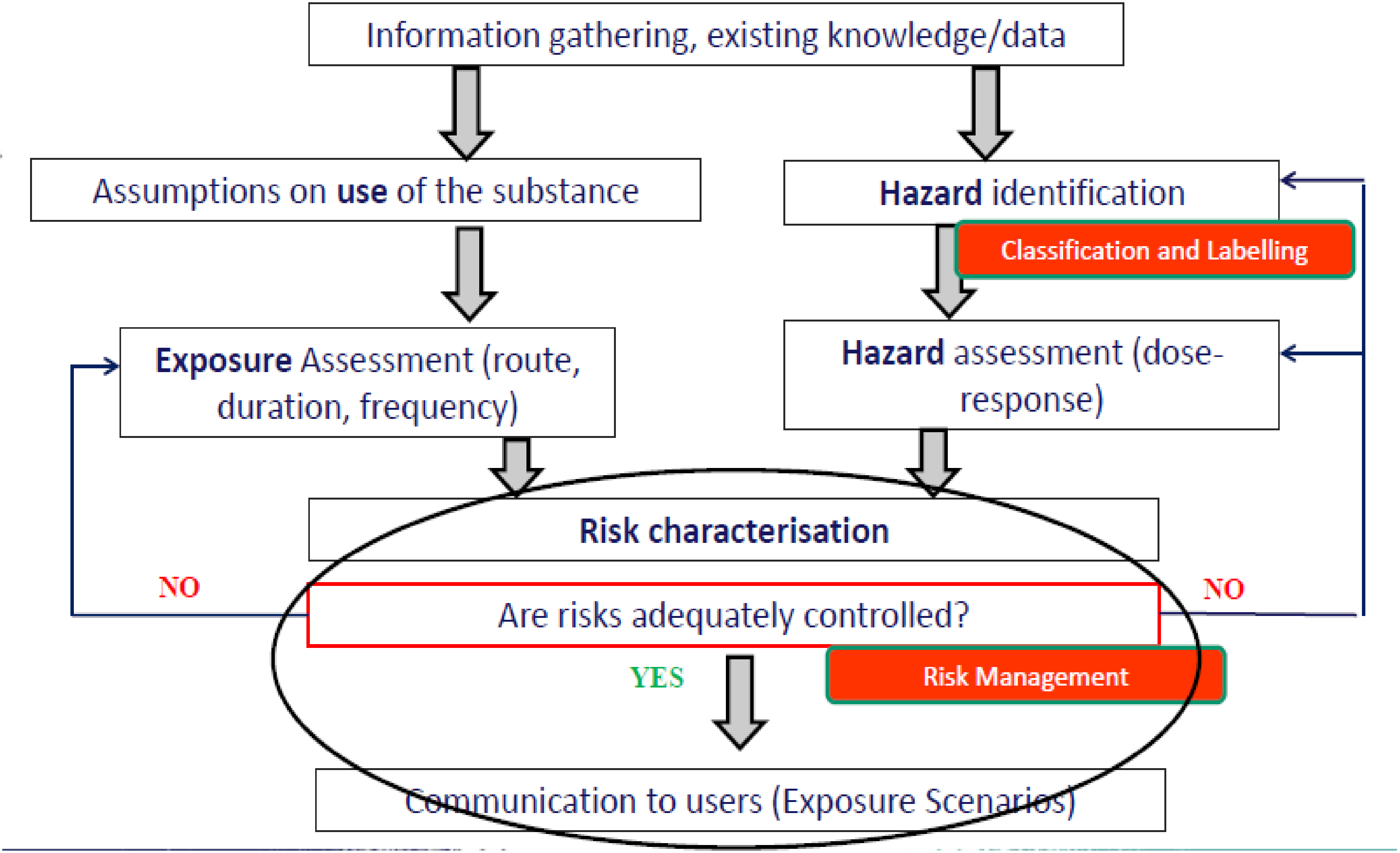
Risk Characterization



Information gathering, existing knowledge/data

Assumptions on **use** of the substance

Hazard identification

Classification and Labelling

Exposure Assessment (route, duration, frequency)

Hazard assessment (dose-response)

Risk characterisation

NO

Are risks adequately controlled?

NO

YES

Risk Management

Communication to users (Exposure Scenarios)

Cont.,

- This combines the results of hazard assessment (effects assessment) and exposure assessments to describe the probability of adverse human health effects

- **Three possible 'generic' conclusions:**

1. There is a need for further information and/or testing
2. There is at present no need for further information and/or testing and no need for risk reduction measures beyond those that are already being applied.
3. There is a need to limit the risks; risk reduction measures that are already being applied will be taken into account

Cont.,

How?

Compare effects concentrations to exposure levels for the various exposed populations (workers, consumers, general population exposed via the environment) for the different exposure routes

$$\boxed{\text{Risk} = \frac{\text{Exposure level}}{\text{Effect level}}}$$

- If exposure level > effect level = risk
- If exposure level < effect level = no risk

Cont.,

- ☐ **Margin of Safety MOS** (or margin of exposure): Ratio of the no-observed-adverse-effect level (NOAEL) for the critical effect to the theoretical, predicted, or estimated exposure dose or concentration

$$\mathrm{MOS} = \frac{\mathrm{NOAEL}}{\text{exposure concentration}}$$

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Risk Management

- Based on information obtained from the **risk assessment, decisions are made regarding the** best way to address contamination and exposure
- The risk manager also includes an evaluation of social, legal, economic and policy issues in order to determine the best approach to address an exposure issue.

Risk Management

- ☐ There are different ways to control the risks associated with hazardous chemicals
- ☐ Some control measures are more effective than others
- ☐ Control measures can be ranked from the highest level of protection and reliability to the lowest *hierarchy of control*.

- ❑ **First step: aim to eliminate a hazard and associated risk**
  - ➢ removing the hazard or hazardous work practice from the workplace
  - ➢ most effective control measure
  - ➢ always to be considered before other control measures

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If this is not reasonably practicable, minimise the risk by:

- **Substitution** (replacement of a hazardous chemical with a chemical that is less hazardous, e.g. use a less volatile material to control a vapour hazard)
- **Isolation separating** people from the chemicals or hazards by distance or barriers to prevent or minimise exposure. Examples of isolation include closed systems, placing workers in cabins, etc.
- **Implementing engineering controls.**
- If a risk still remains, **it must be minimised by implementing administrative controls,** and any remaining risk must be minimised with suitable personal protective equipment (PPE).

❑Environmental chemistry and Toxicology

(Chem 3114).

- ➢Course to be offered; to Chemistry BSc students
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Chapter 6

Introduction to Green Chemistry

- What is Green Chemistry?

- **Describe how Green chemistry minimizes the hazards of some chemical products?**

Green chemistry

- **Green chemistry** is the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances.
- Green chemistry applies across the life cycle of a chemical product, including its design, manufacture, use, and ultimate disposal.
- Green chemistry is also known as sustainable chemistry.

Green chemistry

- it is an area of **chemistry** and **chemical**-engineering focused on the designing of products and processes that minimize the use and generation of hazardous substances.
- a new reality for chemistry and engineering by asking chemists and engineers **to design chemicals, chemical processes and commercial products** in a way that, **at the very least, avoids the creation of toxics and waste**.

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Cont.,

- Through the practice of green chemistry, we can create alternatives to hazardous substances we use as our source materials.
- We can design chemical processes that reduce waste and reduce demand on diminishing resources.
- We can employ processes that use smaller amounts of energy.
- We can do all of this and still maintain economic growth and opportunities while providing affordable products and services to a growing world population.
- **This is a field open for innovation, new ideas, and revolutionary progress.**
- **This is the future of chemistry.**
- **This is green chemistry.**

Definitions

- ***Green chemistry*** is a pro-active approach to pollution prevention.
- It targets pollution at the design stage, before it even begins.
- If chemists are taught to develop products and materials in a manner that does not use hazardous substances, then much waste, hazards and cost can be avoided.
- Green Chemistry is designing chemical products and processes that reduce or eliminate the use and/or the generation of hazardous substances.

Cont.,

- Traditional approaches to pollution prevention focus on mitigating the hazard or **end-of-pipe pollution prevention controls.**
- These traditional technologies focus on limiting the *exposure* of a hazardous material. Unfortunately, exposure precautions can and will fail (i.e., gloves can tear, goggles can break, chemical releases can occur).
- Green chemistry goes to the root of the problem and aims to eliminate the hazard itself.
- The simple equation of risk:

Risk = Hazard x Exposure.

What is the relation between Environmental Science and Green Chemistry?

- **They are complimentary to each other.**
- Environmental Science identifies sources, elucidates mechanisms and quantifies problems in the earth's environment.
- Green Chemistry **seeks to solve these problems by creating alternative, safe technologies.**
- Green Chemistry is *not* Environmental Chemistry. Green Chemistry **targets pollution prevention at the source**, during the design stage of a chemical product or process, and thus prevents pollution before it begins.

How green chemistry differs from cleaning up pollution

- ☐ Green chemistry **reduces pollution at its source** by minimizing or eliminating the hazards of chemical feedstocks, reagents, solvents, and products.

- ☐ This is unlike **cleaning up pollution (also called remediation), which involves treating waste streams (end-of-the-pipe treatment**) or cleanup of environmental spills and other releases.

Is Green Chemistry more expensive than traditional Chemistry?

- Disposal, treatment and regulatory costs associated with the buying, using and generating hazardous materials involves numerous hidden costs.
- When you buy and use a hazardous material you are **paying for it twice**, once when you use it and once when you get rid of it.
- It makes sense that if you use materials that are non-hazardous and thus have minimal regulatory or disposal costs associated with them, the benefit to the economic bottom line is obvious.

Cont.,

- ❑Green Chemistry has provided that, industry has not only accomplished **goals of pollution prevention, but has achieved significant economic benefits simultaneously.**

- □ ***How Chemists are taught Green Chemistry?***

- ❖One way that chemists are learning how to do Green Chemistry is by following the **12 principles** of Green Chemistry.

- ➢They are a set of guidelines that chemists use in order to perform chemistry in a better way.

- ➢As you take a closer look at them, you will find they are very intuitive and simply good practice.

The twelve Principles of Green Chemistry

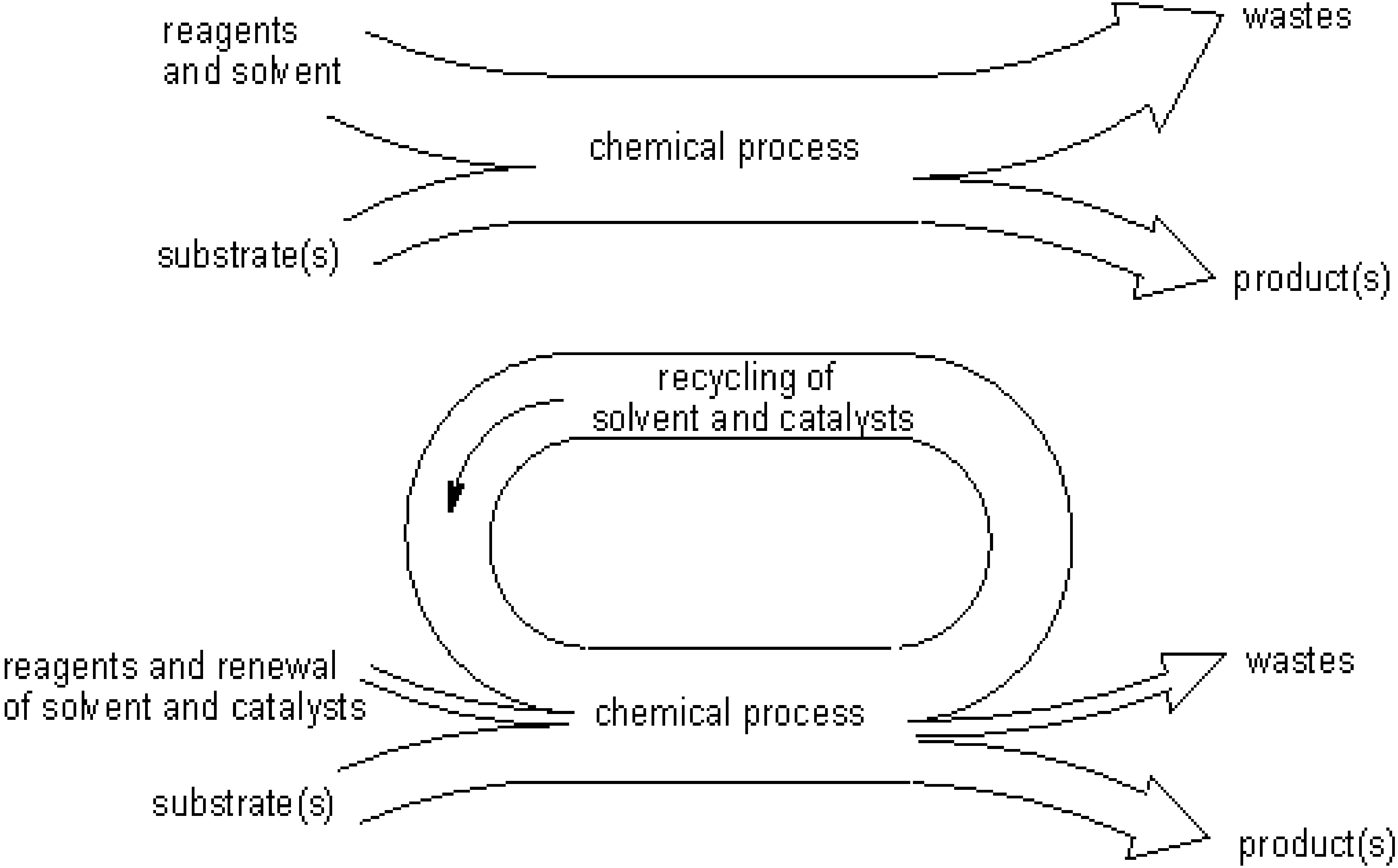
1. *Prevention*

- This principle is the most obvious and over-arches the other principles.
- It goes back to the old proverb ***“an ounce of prevention is worth a pound of cure”***.
- It is better to prevent waste than to treat or clean it up after-the-fact (it has been created)

"It is better to prevent waste than to treat or clean up waste after it is formed"

2. Atom Economy

- This principle gets into the actual chemistry of how products are made.
- As chemists, atoms are assembled to make molecules.
- The molecules are assembled together to make materials.
- This principle states that it is best to use all the atoms in a process. And, those atoms that are not used end up as waste.
- Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
- The atom economy is a simple calculation that can be used when teaching stoichiometry and chemical reactions.
- **The calculation is:**
  - A.E. = Formula Weight (FW) of Product divided by the FW of all of the reactants.
  - It is a simple measure of the amount of waste in a process.



reagents and solvent

chemical process

substrate(s)

wastes

product(s)

recycling of solvent and catalysts

reagents and renewal of solvent and catalysts

chemical process

substrate(s)

wastes

product(s)

3. Less Hazardous Chemical Synthesis

- This principle is focused on *how* we make molecules and materials.
- The goal is to reduce the hazard of the chemicals that are used to make a product (the reagents).
- Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

4. Designing Safer Chemicals

- This principle focuses on the *product* that is made. **Everyone wants safe products.**
- This principle is aimed at designing products that are safe, non-toxic and efficient.
- **A good example of this is pesticides**; which are products that are designed to be toxic.
- Many researchers are focused on created pesticides that are highly specific to the pest organism, but non-toxic to the surrounding wildlife and ecosystems.

5. Safer Solvents and Auxiliaries

- Many chemical reactions are done in a solvent.
- This principle focuses on creating products in such a way so that they use less hazardous solvents (such as water).
- We use solvents regularly in our daily lives (cleaning products, nail polish, cosmetics, etc.) and in the chemistry laboratory.
- The solvents traditionally used have potential toxicity and are certainly not pleasant to smell

6. Design for Energy Efficiency

- Today there is a focus on **renewable energy and energy conservation.**
- We use energy for transportation purposes and to provide electricity to our homes and businesses.
- Traditional methods for generating energy have been found to contribute to global environmental problems such as Global Warming and the energy used can also be a significant cost.
- This principle focuses on creating products and materials in a highly efficient manner and reducing the energy associated with creating the products, therefore **reducing associated pollution and cost**.

7. Use of Renewable Feedstocks

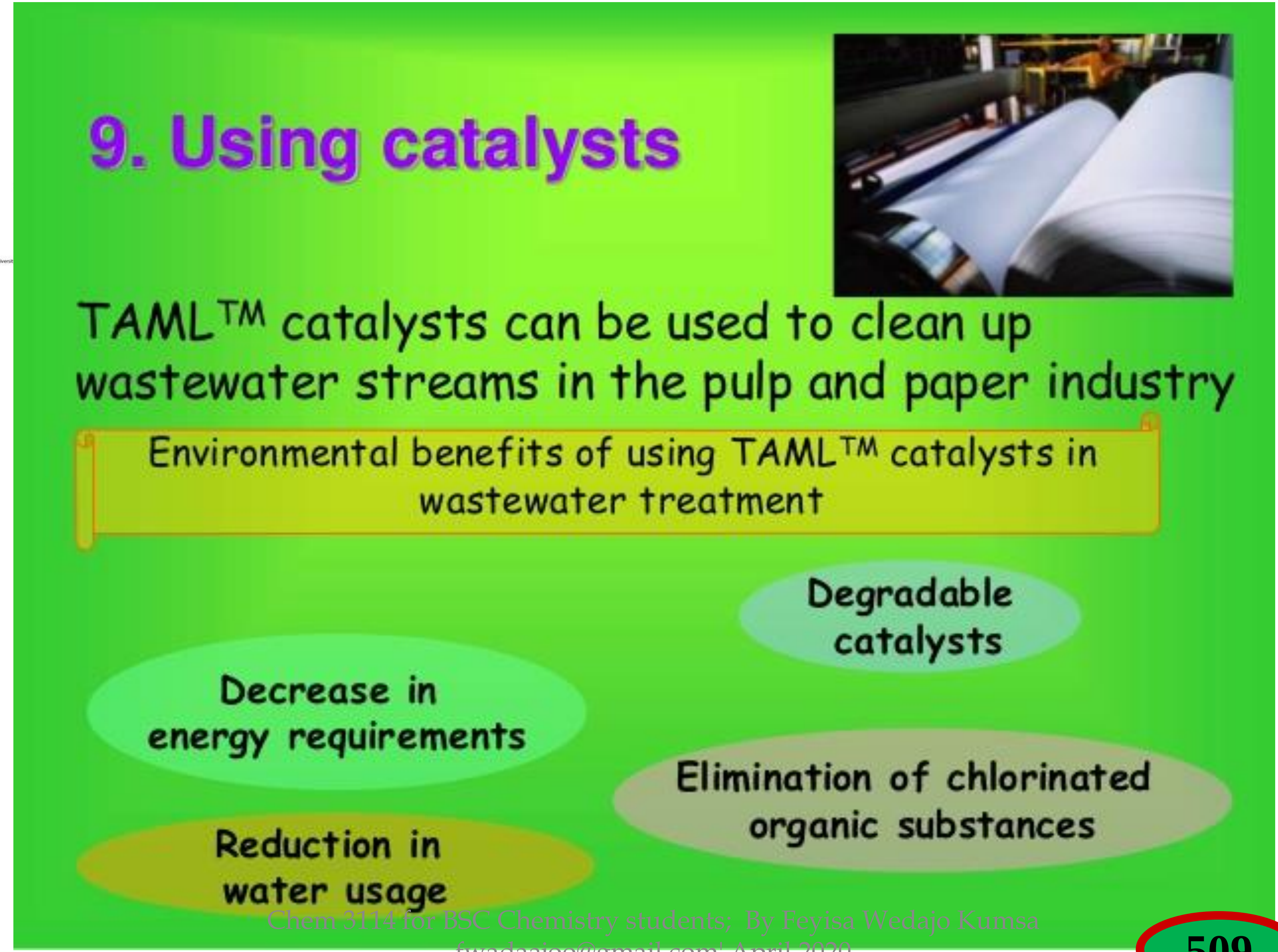
- 90-95% of the products we use in our everyday lives are made from **petroleum.**
- This principle seeks to shift our dependence on petroleum and to make products from renewable materials that can be gathered or harvested locally.
- ***Biodiesel*** is one example of this where researchers are trying to find alternative fuels that can be used for transportation.
- Another example is alternative, bio-based plastics. **PLA** (polylactic acid) is one plastic that is being made from renewable feedstocks such as corn and potato waste.

8. Reduce Derivatives

- This principle is perhaps the most abstract principle for a non-chemist.
- The methods that chemists use to make products are sometimes highly sophisticated.
- And, many involve the manipulation of molecules in order to shape the molecules into what we want them to look like.
- This principle aims to simplify that process and to look at natural systems in order to design products in a simplified manner.

9. Catalysis

- In a chemical process catalysts are used in order **to reduce energy requirements** and to make reactions happen more efficiently (and many times quicker).
- Enzymes are wonderful examples of catalysts that have been proven to perform amazing chemistry
- Green chemists are investigating using enzymes to perform chemistry in the laboratory **in order to obtain the desired product.**
- **Many times enzymes will have reduced toxicity, increased specificity and efficiency.**



9. Using catalysts

TAML™ catalysts can be used to clean up wastewater streams in the pulp and paper industry

Environmental benefits of using TAML™ catalysts in wastewater treatment

Degradable catalysts

Decrease in energy requirements

Elimination of chlorinated organic substances

Reduction in water usage

10. Design for Degradation

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- Not only do we want materials and products to come from renewable resources, but we would also **like them to not persist** in the environment.
- There is no question that many products we use in our daily lives are **far too persistent**.
- **Plastics do not degrade** in our landfills and pharmaceutical drugs such as antibiotics build up in our water streams.
- This principle **seeks to design products** in such a way so that they perform their intended function and then, when appropriate, will degrade into safe, harmless by-products when they are disposed of.

11. Real-time Analysis for Pollution Prevention

- This process is similar to what chemists have to do when they make products.
- How long do they allow the reaction to run for? When do they know it will be done?
- If there was a way to see inside the reaction and to know exactly **when it would be done, then this would reduce waste in the process and ensure that your product is —done** and is the right product that you intended to make.

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12. Inherently Safer Chemistry for Accident Prevention

- This principle focuses on **safety for the worker** and the surrounding community where an industry resides.
- It is better to use materials and chemicals that will **not explode, light on fire, ignite in air**, etc. when making a product.
- There are many examples where safe chemicals were not used and the result was disaster.
- **Example:** The most widely known and perhaps one of the most devastating disaster was that of Bhopal, India in 1984 where a chemical plant had an accidental release that resulted in thousands of lives lost and many more injuries.

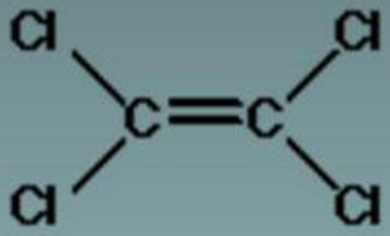
Green Chemistry Is About

Reducing

- Waste
- Material
- Hazard
- Risk
- Energy
- Cost

Green chemistry:

- Prevents pollution at the molecular level
- Is a philosophy that applies to all areas of chemistry, not a single discipline of chemistry
- Applies innovative scientific solutions to real-world environmental problems
- Results in source reduction because it prevents the generation of pollution
- Reduces the negative impacts of chemical products and processes on human health and the environment
- Lessens and sometimes eliminates hazard from existing products and processes
- Designs chemical products and processes to reduce their intrinsic hazards



EXAMPLES OF GREEN CHEMISTRY

Safer dry cleaning

Replace chlorinated solvents like perchloroethylene (perc) with liquid carbon dioxide (CO_2)

Chapter Summary

❖ The concepts of Green Chemistry and the 12 principles of Green Chemistry are summarized as follows:

❑ ***Green chemistry*** is a pro-active approach to pollution prevention. It targets pollution at the design stage, before it even begins.

- ✓ **Prevention.** It is better to prevent waste than to treat or clean up waste after it is formed.
- ✓ **Atom Economy.** Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
- ✓ **Less Hazardous Chemical Synthesis.** Whenever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

Cont.,

- ✓ **Designing Safer Chemicals.** Chemical products should be designed to preserve efficacy of the function while reducing toxicity.
- ✓ **Safer Solvents and Auxiliaries.** The use of auxiliary substances (solvents, separation agents, etc.) should be made unnecessary whenever possible and, when used, innocuous.
- ✓ **Design for Energy Efficiency.** Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.
- ✓ **Use of Renewable Feedstocks.** A raw material or feedstock should be renewable rather than depleting whenever technically and economically practical.

Cont.,

- ✓**Reduce Derivatives.** Unnecessary derivatization (blocking group, protection/deprotection, and temporary modification of physical/chemical processes) should be avoided whenever possible.
- ✓**Catalysis.** Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
- ✓**Design for Degradation.** Chemical products should be designed so that at the end of their function they do not persist in the environment and instead break down into innocuous degradation products.

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THE END !!!!!!!!!!!!

THANK YOU ALL!