:: EXERCISES ::

Q. 1. Tick (√) marks the correct answer:

1) Which of the following can be called contaminant?

a) CO   b) SO_2 c) Ar   d) Cl_2

2) D.O. value of a water sample was found to be 3.5 ppm. This can also be expressed as...

a) 3.5 μg /cm^3 b) 3.5 mg /l   c) 0.35 %   d) 35 ppt

3) Source of lead pollution is...........

a) lead chloride   b) lead bromide   c) leaded gasoline   d) galena

Q.2. State True or False

1) CO released from auto exhaust is a contaminant.
2) Environmental Chemistry is an interdisciplinary subject.
3) Mercury enters in human body through food chain.
4) Some marine organisms are poisonous as they contain arsenic
5) BOD is an empirical parameter of water quality
6) Hydrological cycle is driven by Solar energy and gravitational force.

Q.3. Attempt in brief the followings

1) Illustrate with example the significance of speciation of a pollutant.
2) Explain the term Environment and describe the segments of environment briefly.
3) Name the segments of environment.
4) Name any two parameters used to indicate extent of pollution of water, also give units used to express them.
5) Explain the term 'Pathway of pollutant' by giving example.
6) T.L.V. for Be is 0.002 mg /cm^3. Express the value in ppm.
7) Distinguish between pollutant and contaminant
8) Give the relation between ppm and ppb
9) Explain with diagram the Oxygen cycle
10) Explain with diagram the Sulphur cycle
11) Explain with diagram the Phosphorus cycle
12) Explain with diagram the Nitrogen cycle
13) Explain with diagram the Hydrological cycle
14) Write the importance of hydrological cycle
15) Name the organisms involved in Biological Nitrogen fixation
16) Write in detail the classification of pollutants
17) Explain the scope and importance of Environmental chemistry

Q.4) Define the following terms:

1) Receptor	2) Sink	3) Pollutant
4) Contaminant	5) BOD	6) COD
7) TLV	8) Residence time	9) Ammonification
10) Deamination	11) Nitrification	12) Nitrogen fixation
13) Biogeochemical cycles		

1. Concepts and Scope of Environmental Chemistry.

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Syllabus: Introduction, Environmental pollution and classification, units of concentration, Segments of environment, Biogeo-chemical cycles of C, N, P, S and O system. (06 lectures)

* Introduction :→

Environmental chemistry is the science of chemical interactions in the environment. It is a systematic investigation of chemical species found in air, water and soil, with emphasis on their sources, interactions and transportation as well as their impact and fate in the environment. Environmental chemistry is also the art of using chemical principles to improve the environment and promote long-term development. During the past five decades the world witnessed a series of environmental calamities that include mercury poisoning from contaminated seafood (Japan 1953), recurrence of killer smog (London 1950, 1957), Bhopal gas tragedy (India 1984) and several others where human activities found to be responsible. Basic knowledge of many scientific disciplines including Physics, Biology, Geography and statistics is required to understand the principles of environmental chemistry.

Environmental chemistry is an interdisciplinary subject that encompasses atmospheric, aquatic and soil chemistry as well as relying significantly on analytical chemistry and being linked to other field of study. Environmental chemistry helps to develop methods and procedures to reduce the contaminants or the chemicals in the air, water and soil.

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* Environmental Pollution and classification :→

Pollution of the environment is the undesirable alteration of our environment caused primarily by human activity. Pollution is defined as the introduction of dangerous materials into the environment, resulting in negative changes. Pollution of the environment is one of the most serious ecological crises we face today.

Numerous issues such as environmental quality, ecological imbalance, ozone hole, disruption of earth's natural ecosystems, global warming, green house effect, loss of biological variety, deforestation, desertification, chlorofluorocarbons and acid rains have been discussed.

* Classification of Pollutants :→

Pollutants is a physical or biotic component which adversely alters the environment by altering growth rate of species, interferes with food chain, health, comfort and basic amenities of man. It is an undesirable harmful solid, liquid or gaseous substance present in such a concentration in the environment, which is determined to the whole living biota. The common pollutants are deposited matter like smoke, soot, tar, dust, gases like carbon monoxide, carbon dioxide, sulphur dioxide, chlorine, ozone, ammonia etc. Chemical compounds like aldehydes, acids, arsines, phosgene, toxic metals like cadmium, mercury, lead, iron, Zinc, Pesticides, biocides, radio-nuclides like argon-41, cobalt-60 etc.

* **Classification on the basis of their existence in the environment:**

(i) Primary Pollutants: The pollutants emitted directly from an identifiable source and exit as such after their release. e.g. SO_x and NO_x.

(ii) Secondary Pollutants: Chemical reactions produce these pollutants which are generated from primary pollutants. e.g. hydrocarbons and nitrogen oxides react in presence of sunlight to form peroxy acetyl nitrate (PAN) as a secondary pollutant.

* **Classification on the basis as follows from the perspective of the ecosystem:→**

(i) Biodegradable pollutants: Micro-organisms totally degrade contaminants such as home garbage and sewage.

(ii) Non-biodegradable pollutants: Toxic metals, herbicides, pesticides and different chemicals.

* **Classification on the basis of as persistent:→**

(i) Persistent pollutants:→ Some pollutants are not easily biodegradable and remain unchanged in the environment for longer time they are called persistent pollutants. e.g. Plastics, certain pesticides, mercury, lead, radio-active waste etc.

(ii) Non-persistent pollutants:→ These pollutants do not persist in the environment but they break down into simpler substances in a short period of time and get mixed with soil. e.g. Agricultural waste, garbage etc.

* **Classification on the basis of their origin:→**

(i) Natural Pollutant: e.g. volcanic eruptions.

(ii) Anthropogenic pollutants: e.g. Emissions from industries, pesticides, fertilizers etc.

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* Terminology :→

① **Pollutant** :→ Pollutants are anything in the environment that is alive or non-living or any physical agent that is detected above a specific level that is harmful to human, plant, animal and other materials. e.g. CO_2, SO_2, Pb, H and fuel combustion.

② **Contaminant** :→ It is a material that does not occurs naturally but is introduced into the environment by human activities and alters its composition. e.g. Cl_2 gas, methyl isocynaide (MIC) etc.

③ **Source** :→ It is origin of a pollutant e.g. combustion of leaded gasoline is a source of lead in the atmosphere. Coal combustion is one of the major sources of SO_2 in the atmosphere.

④ **Receptor**: It is everything that is harmed by a pollutant e.g. Man is receptor for photo-chemical smog, which irritates the eyes and respiratory tract.

⑤ **Sink** :→ A sink is medium that retains and interact with a long-lived chemical species usually a pollutant. e.g. A marble structure acts as a sink for ambient H_2SO_4 acid and is eventually damaged as a result of the interaction.

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2$$

⑥ **Pathway of Pollutant** :→ It is the technique or way through which that pollutant is disseminated from its source into various parts of the environment. e.g. Organomercury compounds as fungicides →

Animals ← Food chain ← Mercury compounds in soil ← sowing Fungicide dressed seeds.

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(7) Speliation :→ It refers to the process of identifying a pollutants chemical form i.e. species in the environment. Toxicity varies depending on the pollutants species eg. the pollutant Hg is found as Hg^0, Hg^{2+}, CH_3Hg^+ and $(CH_3)_2Hg$.

(8) Dissolved oxygen :→ (D.O.) : It refers to the amount of oxygen in a water sample that is dissolved. The level of D.O. is measured in milligram of oxygen per litre. Unpolluted fresh water has a D.O. level of 4-6 ppm.

(9) Chemical oxygen demand :→ (C.O.D.) : It is amount of Chemically accessible oxygen needed to completely oxidise organic materials in polluted water. Chemical oxidation of a water sample with Potassium dichromate in 50% H_2SO_4 acid is used to measure the amount of organic materials in water.

(10) Biological oxygen demand :→ (B.O.D.) : The amount of oxygen consumed in the biodegradation of organic matter in water during a 5 day period is refered to as the B.O.D. value. The B.O.D. value is measured in ppm of oxygen. The greater the B.O.D. value, the more polluted water sample. The domestic sewage has a B.O.D. value of 165 ppm, while treated domestic sewage has a B.O.D. 25 ppm.

(11) Threshold limit value :→ (T.L.V.) : It specify the maximum amount of harmful contaminant in the atmosphere to which a healthy industrial worker can be exposed for an eight hour without suffering any negative consequences.

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(12) Residence time :→ The residence time of a chemical species is the amount of time that it spends in a certain environment without changing its chemical form.

* Units of Concentration :→

For liquid and solid samples are measured as

1 PPM = 0.0001% = 100 pph = 1000 ppb = 10,00,000 ppt.

1 L water = 10^3 ml water = 10^3 gm of water = 10^6 mg H_2O

∴ 4 PPM D.O. = 4 mg D.O. per 10^6 mg water = 4 mg D.O. per 1 litre water.

For expressing concentration of gaseous samples is mass per unit volume usually 'microgram per cubic metre of air, $\mu g/m^3$.

* Segments of Environment :→

The environment consists of four segments such as Atmosphere, Hydrosphere, Lithosphere and Biosphere.

(I) Atmosphere :→ It is the protective blanket of gases surrounding the earth which sustains life on earth and saves it from the hostile environment of outer space. It absorbs most of the cosmic rays from outer space and a major portion of electromagnetic radiation from the sun. The atmosphere screens the dangerous ultra-violet radiations from the sun and transmits only near ultraviolet, visible, near infra red radiations and radio-waves. The atmosphere comprises of a

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mixture of gases like N_2, O_2, CO_2, Ar etc. and extends upto 500 kms above the earth surface. A constant exchange of matter takes place between the atmosphere, biosphere and hydrosphere.

The weight of atmosphere is nearly 5×10^{15} metric tonnes- which is about one millionth of the total weight of the earth. The atmospheric temperature, pressure and density vary considerably with atitude. The atmospheric temperature varies from $-100\,^{\circ}C$ to $+1200\,^{\circ}C$ depending upon the altitude. The atmosphere pressure at sea level is 1 atmosphere, while at 100 km above sea level it drops to 3×10^{-7} atmosphere. Its density at the surface of earth is about 0.0013 gm per cubic metre which decreases sharply with increasing altitude and gradually thins out into space. At about 600 kms and above the atoms and molecules describe free elliptical orbits in the earth's gravitational field.

The atmosphere plays a vital role in maintaining the heat balance on the earth by absorbing the infra red radiations received from the sun and re-emitted by the earth. In fact, it is the green house effect which keeps the earth warms enough to sustain life on the earth. The important gaseous constituents of the earth such as O_2, N_2, CO_2 play important role in sustaining life on earth. O_2 supports life on earth. Nitrogen is an essential macro-nutrient for plants. CO_2 is essential for photosynthetic activity of plants.

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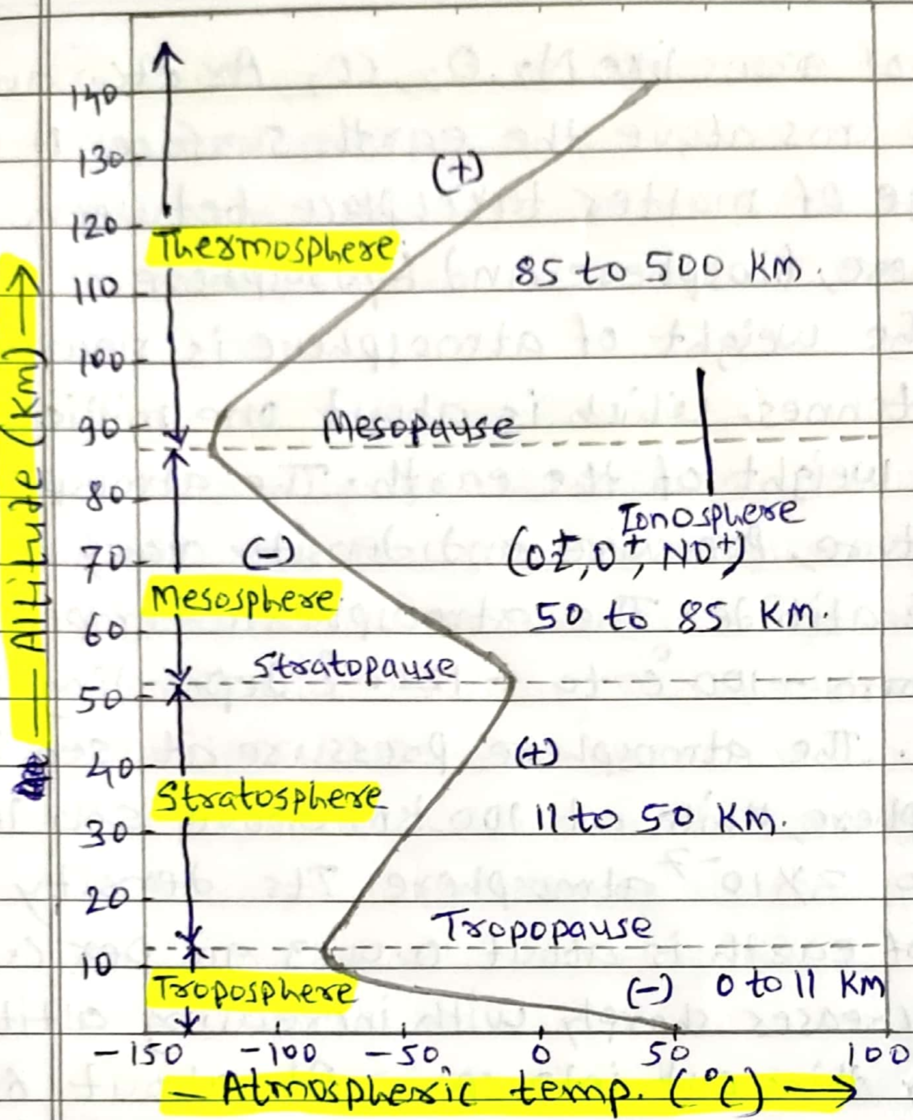

Fig. Regions of atmosphere:

Atmosphere can be broadly divided into four regions. (i) Troposphere.

(ii) Stratosphere.

(iii) Mesosphere.

(iv) Thermosphere.

(i) Troposphere :→ It is the region nearest to the earth's surface and extends upto an altitude of 11 Km. The upper limit may vary upto 20 Km depending upon temperature and nature of terrestrial surface. Troposphere accounts for over 70 % of the atmospheric mass.

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It is the most important zone for organisms and composed of mainly O_2, N_2, CO_2, H_2O and Particulate matter. The composition of air in this region remains more or less constant in the absence of any significant air pollution. The average temperature in the troposphere is about 14°C. The top of troposphere is called tropopause. The change of temperature with height is known as lapse rate. The decrease of temp. with increasing altitude in the troposphere is called positive lapse rate. The transition from positive lapse rate to negative lapse rate at the tropopause marks the temperature inversion.

(ii) Stratosphere :-> The region above the tropopause is known as stratosphere from 11 km to 50 km with temperature range from −56 to −2°C. In this region the temp. altitude curve shows a warming trend with increasing altitude i.e. it exhibits a negative lapse rate. Ozone is responsible for the −ve lapse rate. The region above the stratosphere is called stratopause which is the second transitional layer that is relatively warm.

(iii) Mesosphere :-> It is the region above the stratosphere i.e. stratopause that extends from 50 km to 85 km. In this zone the temp. again decreases with height i.e. it exhibits a positive lapse rate. The temp. at the top of mesosphere reaches from −2°C to about −92°C. Immediately above the mesosphere is another transitional layer called mesopause.

(iv) Thermosphere :-> It is the region from 85 to 500 km, temp. ranges from −92°C to 1200°C,

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~~region~~ immediately above the mesopause, where the temp. rises very rapidly with increasing altitude, exhibiting a –ve lapse rate. This region is characterised by maximum temp. i.e. 1200 °C, low pressure and low densities. The region above the stratosphere in the altitude range 50 to 100 Km is called ionosphere.

(2) Hydrosphere :-> It includes all the surface and ground water resources i.e. rivers, seas, Oceans, streams, lakes, reservoirs, glaciers, Polar ice caps, water locked in rock-crevices and minerals lying deep below the earth crust. Earth is called the blue planet because about 80% of its surface is covered by water. However, 97% of the earth's water resources is locked-up in seas and oceans which is too saline to drink and for the direct use for industrial and agriculture purposes. Of the remaining 3% about 2.3% is trapped in giant glaciers and polar ice-caps. Thus not even 1% of the total world's water resources is available for exploitation by man for domestic, agriculture and Industrial purposes. Water is an excellent universal solvent. Water is polar molecule. Natural water contains ions such as Na^+, K^+, Mg^{2+}, Cl^-, SO_4^{2-}, PO_4^{3-}, NO_2^-, CO_3^{2-} and HCO_3^- etc.

(3) Lithosphere :-> The mantle of rocks constituting the earth's crust is called lithosphere. The soil covering the rocks is the important part

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of lithosphere. The soil mainly consists of complex mixture of inorganic and organic matter, minerals, air and water. The inorganic minerals constituents include complex mixture of silicates of Na, K, Ca, Al and Fe, oxides of Fe, Mn and Ti and carbonates of Ca and Mg. The organic matter, which is only 5% mainly determines the productivity of the soil. Soil is store house of minerals, reservoir of water, conserver of soil fertility, producer of crops, home of wild life and livestock.

(4) **Biosphere :→** It is the region of earth where life exists and includes a global girdle extending from about 10,000 m below sea level to 600 m above sea level. The biosphere covers the entire realm of living organisms and their interaction with the environment.

* Biogeo-chemical cycles of C, N, P, S and O system:→

(i) Biogeo-chemical cycles of Carbon :→

The carbon cycle is the biogeochemical cycle by which carbon is exchanged among the biosphere, pedosphere, geosphere, hydrosphere and atmosphere of the earth. Carbon is the main component of biological compounds as well as a major component of many minerals such as limestone. Along with the nitrogen cycle and the water cycle, the carbon cycle comprises a sequence of events that are key to make Earth capable of sustaining life. It describes the movement of carbon as it is recycled and reused throughout the biosphere as well as long term processes of carbon

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sequestration to and release from carbon sinks. Carbon sinks in the land and the ocean each currently take up about one quarter of anthropogenic carbon emissions each year.

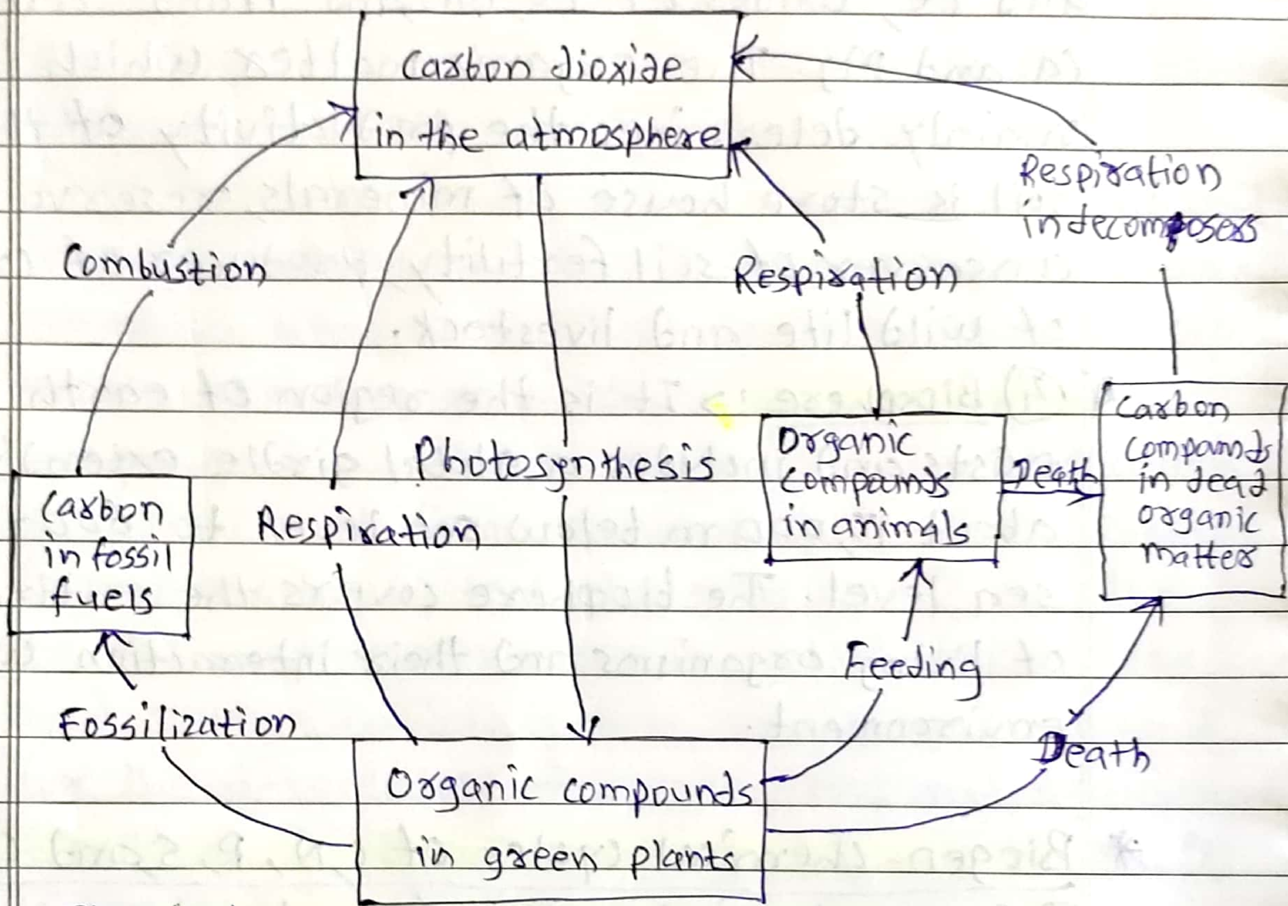

Fig: Carbon cycle:

Human have disturbed the biological carbon cycle for many centuries by modifying land use and ~~moreover~~ with the recent industrial scale mining of fossil carbon from the geosphere. CO_2 in the atmosphere had increased nearly 52% over pre-industrial levels by 2020, forcing greater atmospheric and earth surface heating by the sun. The increased CO_2 has also increased the acidity of the ocean surface by about 30% due to dissolved carbon dioxide, carbonic acid and other compounds and

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is fundamentally altering marine chemistry. The largest consequences to the carbon cycle and to the biosphere which critically enables human civilization are still set to unfold due to the vast yet limited inertia of the Earth system.

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(ii) Biogeo-chemical cycles of Nitrogen :->

The nitrogen cycle is the biogeochemical cycle by which nitrogen is converted into multiple chemical forms as it circulates among atmosphere, terrestrial and marine ecosystems. The conversion of nitrogen can be carried out through both biological and physical processes. Important processes in the nitrogen cycle include fixation, ammonification, nitrification and denitrification. The majority of Earth's atmosphere 78 % is atmospheric nitrogen making it the largest source of nitrogen.

The nitrogen cycle is of particular interest to ecologists because nitrogen availabity can affect the rate of key ecosystem processes, including primary production and decomposition. Human activities such fossil fuel combustion use of artificial nitrogen fertilizers and release of nitrogen in waste water have dramatically altered the global nitrogen cycle. Human modification of the global nitrogen cycle can negatively affect the natural environment system and also human health.

Nitrogen present in the environment in a wide variety of chemical forms including organic nitrogen, ammonium, nitrite, nitrate, nitrous oxide, nitric oxide or inorganic nitrogen gas.

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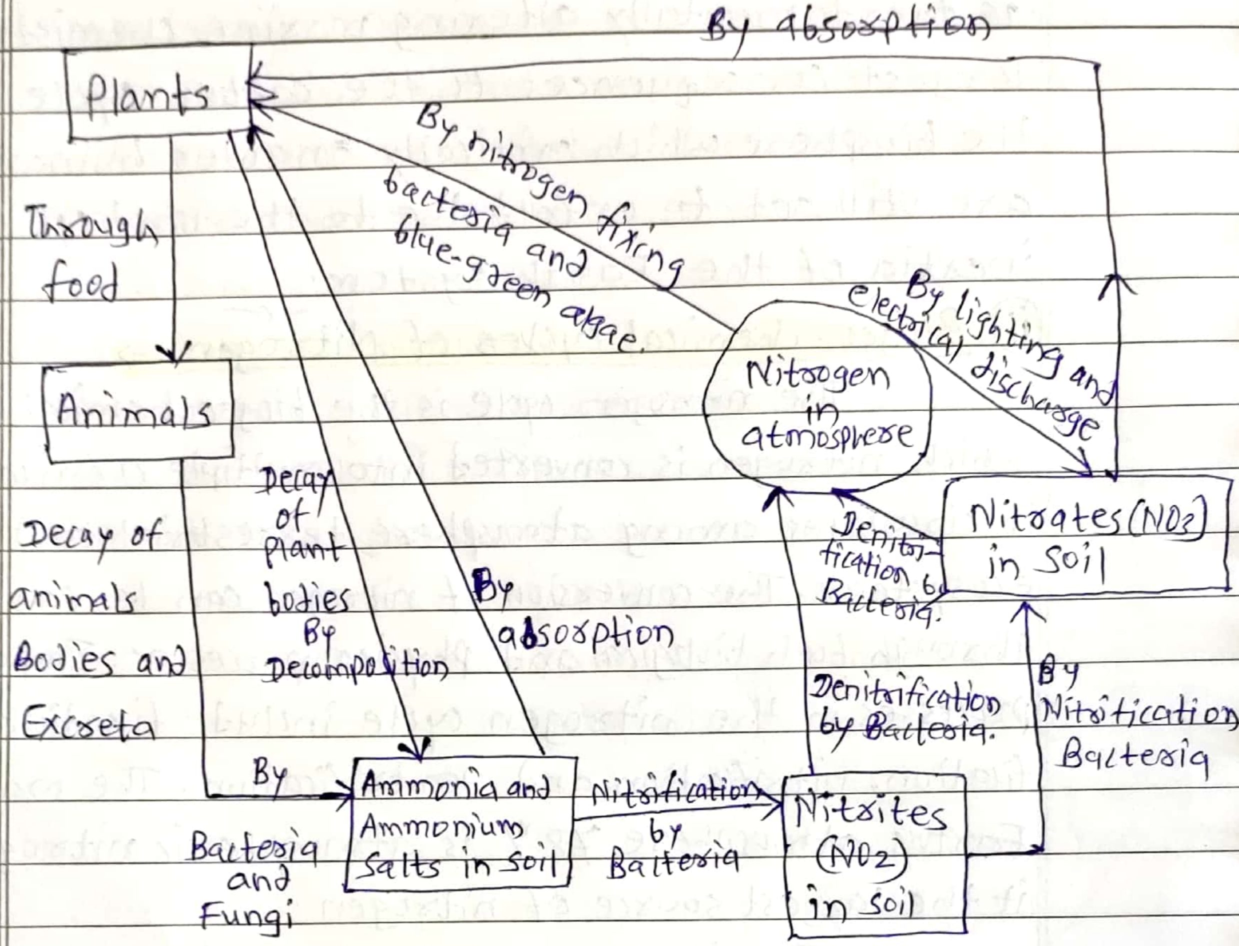

Fig: Nitrogen cycle.

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(iii) Biogeo-chemical cycle of Phosphorus :→

The phosphorus cycle is the biogeochemical cycle that describes the movement of phosphorus through the lithosphere, hydrosphere and biosphere. Unlike many other biogeochemical cycles the atmosphere does not play a significant role in the movement of phosphorus and phosphorus based compounds are usually solids at the typical ranges of temperature and pressure found on earth. The production of phosphine gas occurs in only specialised local conditions. Therefore the phosphorus cycle should be viewed

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from whole earth system and then specifically focused on the cycle in terrestrial and aquatic system.

On the land, Phosphorus gradually becomes less available to plants over thousands of years, since it is slowly lost in runoff. Low concentration of Phosphorus in soils reduces plant growth and slows soil microbial growth. Soil micro-organisms act as both sink and sources of available phosphorus in the biogeochemical cycle.

Humans have caused major changes to the global phosphorus minerals and use of phosphorus fertilizer and also the shipping of food from farms to cities where it is lost as effluent.

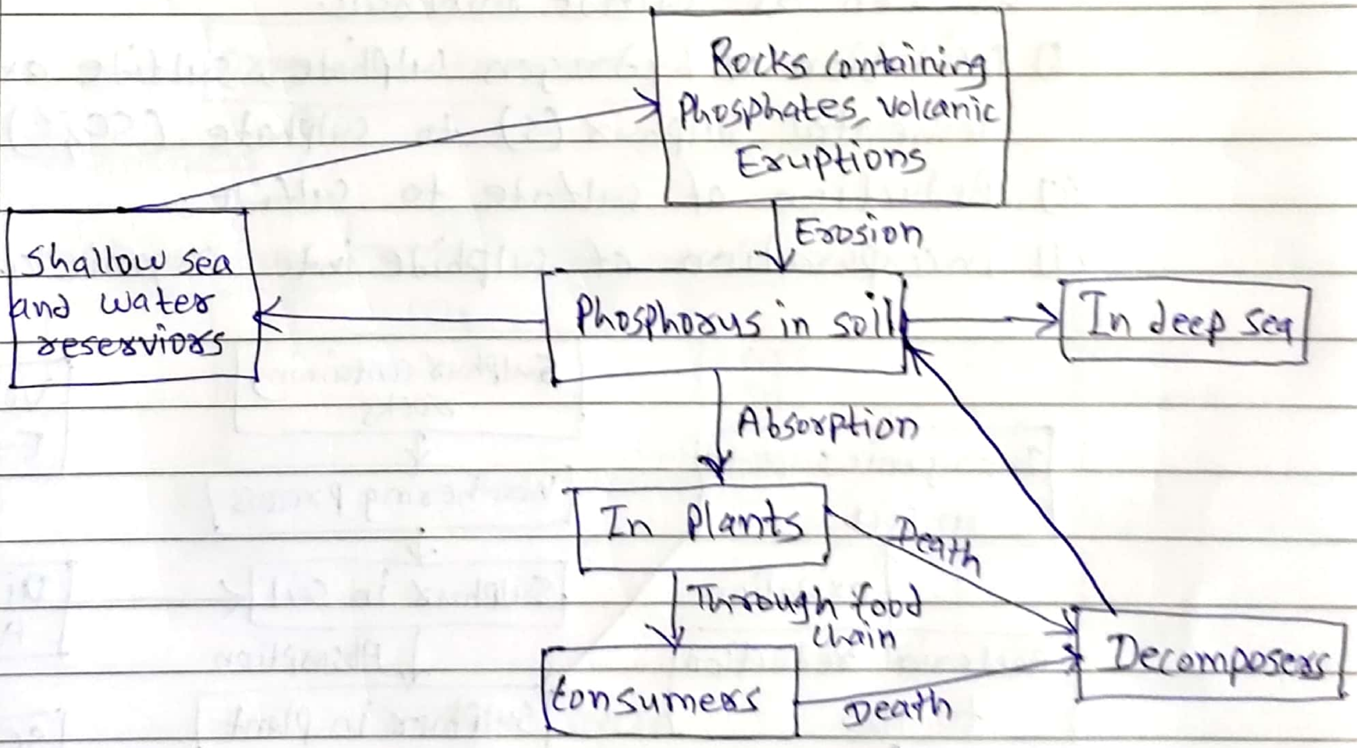

Fig: Phosphorus cycle:

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(IV) Biogeochemical cycle of Sulphur :→

The sulphur cycle is biogeochemical cycle in which the sulphur moves between rocks, water ways and living systems. It is important in geology as it affects many minerals and in life because sulphur is an essential element, being a constituent of many proteins and cofactors and sulphur compounds can be used as oxidants or reductants in microbial respiration. The global sulphur cycle involves the transformations of sulphur species through different oxidation states, which play an important role in both geological and biological processes.

Steps of the sulphur cycle are:

ⓐ Mineralization of organic sulphur into inorganic forms such as hydrogen sulfide (H_2S), elemental sulphur as well as sulfide minerals.

ⓑ Oxidation of hydrogen sulphide, sulfide and elemental sulphur (S) to sulphate (SO_4^{-2}).

ⓒ Reduction of sulfate to sulfide.

ⓓ Incorporation of sulphide into organic compounds.

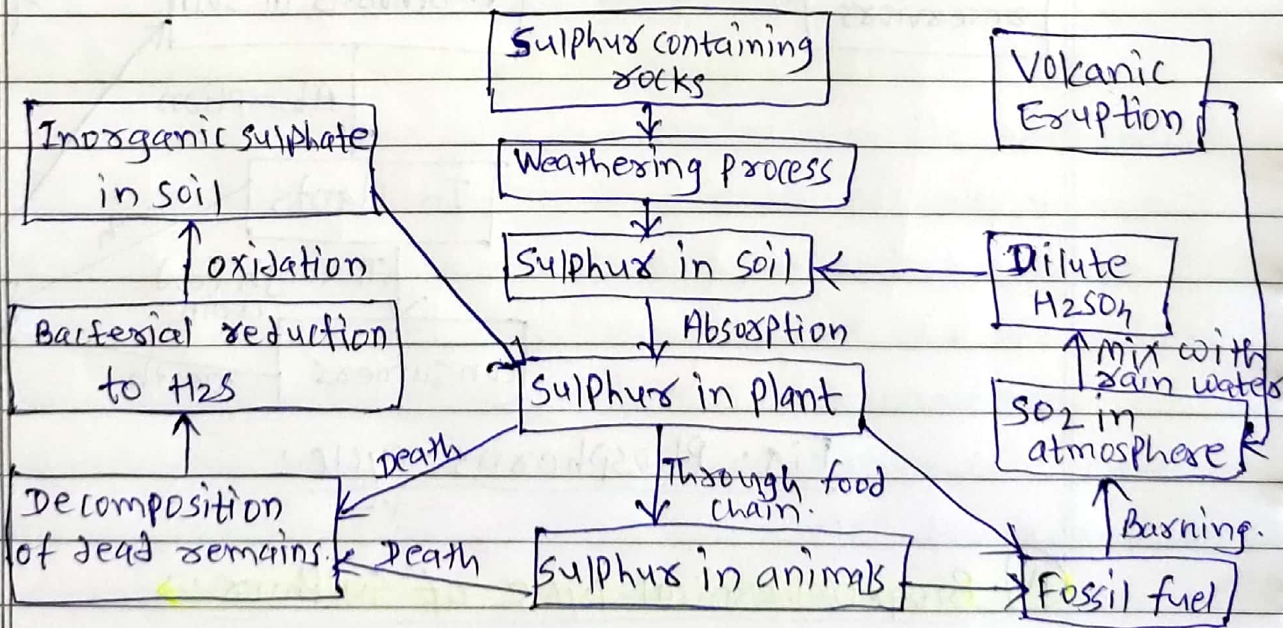

Fig.: Sulphur cycle :->

(v) Biogeochemical cycle of oxygen :->

The oxygen cycle is the biogeochemical cycle of oxygen atoms between different oxidation states in ions, oxides and molecules through redox reactions within and between the spheres/ reservoirs of the planent earth. The word oxygen in the literature typically refers to the most common oxygen allotrope, elemental / diatomic oxygen (O_2) as it is a common product or reatant of many biogeochemical redox reactions within the cycle. Processes within the oxygen cycle are considered to be biological or geological and are evaluated as either a source (O_2 production) or sink (O_2 consumption).

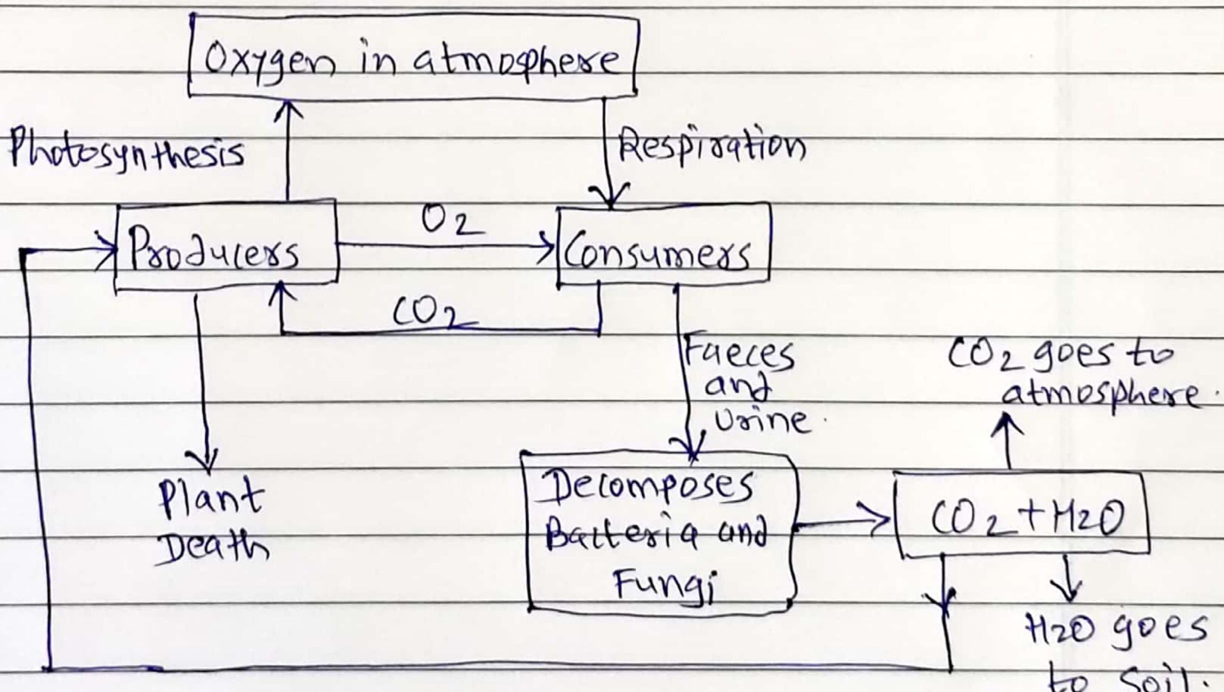

Fig.: Oxygen cycle.

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