

Ministry of Higher
Education and Scientific
Research
University of Baghdad
College of Science
Department of Biology



Advanced Environmental Pollution

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ا.د. عادل مشعان ربيع

Lecture 1

1. Introduction to understanding pollution

What is pollution and why is it important and is it harmful at all levels? What happens to pollutants in the environment? What are the root causes of pollution? What are the effect of pollution on plants, animals and human especially. These are among major questions in this course.

Pollution is the introduction of contaminants into the environment that cause harm to humans or other living organisms, or that damage the environment.

The best introduction to understanding pollution we must give primary idea about new subjects that a strong relation with ecology and pollution, the first is the environmental chemistry which is a branch of chemical science that deals with the production, transport, reactions, effects, and fates of chemical materials in the water, air, terrestrial, and biological environments and the effects of human activities. The definition of environmental chemistry is demonstrated with a typical pollutants. In this case sulfur in coal is oxidized to sulfur dioxide gas that is emitted to the atmosphere. The sulfur dioxide gas can be oxidized to sulfuric acid by atmospheric chemical processes, fall back to Earth as acid rain, affect a receptor such as plants, and end up in a "sink" such as a body of water or soil. While ecotoxicology is the science of contaminants in the biosphere and their effects on constituents of the biosphere, including humans. Or study of impacts of pollutants on the structure and function of ecosystems. The important of pollution is rising from 2 million chemicals are in commercial use. The US EPA has identified large number of these as persistent, bioaccumulative and toxic (PBTs).

Traditionally, environmental science has considered four environmental spheres: water, air, living organisms, and earth.

1.1. Hydrosphere.

This includes all surface and ground water resources (oceans' seas, rivers, stream, lakes, ground water and so forth

1.2. The geosphere (Lithosphere).

This outermost solid layer of the Earth provides a platform for most life-forms. The solid rock bears a shallow layer of soil in which nutrient elements become available to organisms. The surface of the lithosphere is shaped into landforms which provide varied habitats for plants, animals, and humans.

1.3. Biosphere

This is region of the earth where life exists and includes a global belt extending from about 10,000m below sea level to 6000 m above sea level. Most of the biosphere is contained in the shallow surface zone called the life layer. On land, the life layer is the zone of interactions among the biosphere, lithosphere, and atmosphere.

1.4. Atmosphere

The atmosphere comprises of a mixture of gases and extends up to about 500km above the surface of the earth. A constant exchange of matter takes place between the atmosphere, biosphere and hydrosphere . Their relative weights are of the following order:

Biosphere : Atmosphere : Hydrosphere

1 : 300 : 69,100

2. What do we mean by pollutant?

- **Pollutant:** a substance in part as a result of man's activities, and which has a adverse effect on living organisms.
 - **Contaminant:** a substance released by man's activity (not necessarily adverse effect).
- **Xenobiotic:** a foreign chemical not produced in nature and not a constitute component of a specified biological system—usually applied to a manufactured chemical. Or a chemical that is foreign to the biosphere i.e. is not produced by a natural biological or abiotic source.

3. Major classes of pollutant

Many different chemicals are regarded as pollutants, ranging from simple inorganic ions to complex organic molecules. In this subject representatives will be identified of all the major classes of pollutant, and their properties and occurrence will be briefly reviewed.

3.1: Inorganic pollutants

3.1.1: Metals and Metalloids

The definition of the term metals is as follows: Metals are chemical elements with *general* characteristics and similar [physical and chemical properties](#) under normal conditions. Many elements may be classified as metals according to one set of properties and as non-metals according to another. Examples: Lead is very soft. Mercury is a liquid. The periodic table is a reasonable tool for framing our discussion of different inorganic contaminants . The elements in this table can be divided generally into metals, nonmetals, or metalloids (semimetals). Most elements are metals . Pure metals are characteristically solid at room temperature although mercury is the exception. They are described as good electrical and thermal conductors. Elements classified as Metalloids have properties of both metals and non-metals. For example, they can be semiconductors with their electrical conductance increasing with temperature. They can also form strong covalent bonds with some other elements. Examples, Boron , Silicone, Arsenic and Antimony. Normal biological processes can be negatively affected by uptake of metals from the environment. Ecologist's should recognize the characteristics that influence their changes in state (e.g., their oxidation, ionization, and assimilation into organic form) in the environment, and subsequent movements and interactions of the metals.

3.1.2: Anions

There are some inorganic pollutants which are not particularly toxic, but which cause environmental problems because they are used in such large quantities. These include anions such as nitrates and phosphates. Nitrate fertilizers are used extensively in agriculture.

During the growth period of crops, most of the fertilizer applied is absorbed by plant roots. However, when growth ceases, nitrate released during the decomposition of dead plant material passes down through the soil and may enrich closest water bodies. The increase in available nitrogen may cause blooms in algal populations. This effect is called **eutrophication** and eventually leads to oxygen starvation as microorganisms break down the dead algal tissues. The safe limit for nitrates in drinking water in the some countries has been set at 50 parts per million (p.p.m.). A human health problem may arise if young babies ingest

bottled milk made up with nitrate-contaminated water. During their first few months of life, human infants have an anaerobic stomach. The nitrates are converted to nitrites in this oxygen-poor environment. The nitrites bind to haemoglobin, reduce its capacity to carry oxygen and the infant may develop 'blue baby syndrome' or **methaemoglobinaemia**. The problem does not arise with breast-fed babies (definitely a case of 'breast is best!'). Similar problems of eutrophication can also arise with phosphates used as fertilizers. However, there is an additional source: washing powders. In the 1950s and 1960s, it was common to see a huge build-up of foam below dams and waterfalls downstream of the outfalls of sewage treatment works.

3.2: Organic pollutants

The great majority of compounds that contain carbon are described as 'organic', the few exceptions being simple molecules such as CO_2 and CO . Carbon has the ability to enter into the formation of diversity of complex organic compounds, many of which provide the basic materials of living organisms. The reason for this is the tendency of carbon atoms to form stable bonds with one another, thereby creating rings and extended chains. Carbon can also form stable bonds with hydrogen, oxygen and nitrogen atoms. Molecules built of carbon alone (e.g. graphite and diamond) or of carbon and hydrogen (hydrocarbons) have very little polarity and consequently low water solubility. Molecules with a strong charge are described as highly polar; molecules of low charge have low polarity. Polar compounds tend to be water soluble because the charges on them are attracted to opposite charges on water molecules. For example, a positive charge on an organic molecule will be attached to a negative charge on a water molecule. Carbon compounds tend to be more polar and more chemically reactive when they contain functional groups such as OH , HC=O and NO_2 . In these examples, the oxygen atom attracts electrons away from neighbouring carbon atoms, thereby creating a charge imbalance on the molecule.

Molecules of high polarity tend to enter into chemical and biochemical reactions more readily than do molecules of low polarity.

The behaviour of organic compounds is dependent upon their molecular structure—molecular size, molecular shape and the presence of functional groups being important

determinants of metabolic fate and toxicity. Thus, it is important to know the formulae of pollutants in order to understand or predict what happens to them in the living environment. The pollutants that will be described here are predominantly man-made ('anthropogenic') compounds which have appeared in the natural environment only during the last century. This is only a very short time in evolutionary terms, and there has been only limited opportunity for the evolution of protective mechanisms against their toxic effects (e.g. detoxication by enzymes) beyond pre-existing mechanisms acting against 'natural' pollutants.

3.2.1 Hydrocarbons

These are compounds composed of the elements carbon and hydrogen only. Some hydrocarbons of low molecular weight (e.g. methane, ethane and ethylene) exist as gases at normal temperature and pressure. However, the great majority of hydrocarbons are liquids or solids. They are of low polarity (i.e. electrical charge) and, consequently, have low water solubility, but they have high solubility in oils and in most organic solvents. Hydrocarbons are divisible into two classes: (i) non-aromatic hydrocarbons and (ii) **aromatic** hydrocarbons. The distinguishing feature of aromatic hydrocarbons is the presence of one or more benzene rings in their structure. Benzene rings are six-membered carbon structures which are 'unsaturated' in the sense that not all available carbon valences are taken by linkage to hydrogen. Other hydrocarbons do not have this feature. They vary greatly in molecular size and may be fully saturated (e.g. hexane and octane) or unsaturated. Unsaturated hydrocarbons contain carbon—carbon (C—C) **double bonds** (e.g. ethylene) or carbon—carbon **triple bonds** (e.g. acetylene).

The properties of these two groups of hydrocarbons will now be considered separately. The properties of non-aromatic hydrocarbons depend upon molecular weight and degree of unsaturation. The lower members of the series are gases, the higher members liquids or solids. There are many polycyclic aromatic hydrocarbons (PAHs) which are planar (i.e. flat) molecules consisting of three or more six-membered (benzene) rings directly linked together.

The major sources of hydrocarbons are deposits of petroleum and natural gas in the upper strata of the earth's crust. These fossil fuels originate from the remains of plants and animals of earlier geological times (notably the carboniferous period). Although non-aromatic

hydrocarbons predominate in these deposits, crude oils also contain significant amounts of PAHs. PAHs are also formed as a consequence of the incomplete combustion of organic materials. Thus, major sources of hydrocarbon pollution are , oil or petrol are burned, when trees or houses burn and when people smoke cigarettes.

3.2.2: Detergents

Detergents are organic compounds which have both polar and non-polar characteristics, where they are associated with both polar and non-polar media. Detergents are of three types: (i) anionic, (ii) cationic and (iii) non-ionic. The first two types have permanent negative or positive charges and non-ionic detergents have no such permanent charge; rather, they have a number of atoms which are weakly electropositive and electronegative. Detergents are very widely used in both domestic and industrial premises. The major entry point into water is by sewage flow into surface waters. They are also used in pesticide formulations and for dispersing oil spills at sea.

3.2.3: Pesticides

This is a relatively large group of insecticides with considerable diversity of structure, properties and uses. Most organochlorine pesticides and many of the organic chemicals already discussed are classified as persistent organic pollutants (POPs) because they are resistant to degradation in the environment and tend to increase in concentration with movement up through food webs. They can persist at alarming concentrations in biota and many can disperse globally as will be discussed later. Sometimes, POPs are called persistent toxicants that bioaccumulate (PTB) or persistent bioaccumulative toxic (PBT) chemicals. The most widely recognized organochlorine pesticide members of the POPs are aldrin, chlordane, DDD, DDT, and heptachlor.

3.3: Organometallic compounds

Some metal ions are so insoluble that they are relatively non-toxic to animals if ingested. Metals are modified in this way to increase their toxicity for use as pesticides. Organomercury compounds were used widely as antifungal seed dressings in the UK until as recently as 1993. Organolead compounds have been used extensively for control of caterpillars on fruit crops.

Other compounds, particularly tributyl tin, are extremely toxic. Their main use is antifouling paints which are applied to the outer surface of boats and fish cages to inhibit settlement by marine organisms. When these substances leach into the environment, they can affect nontarget organisms. A tragic example of the effects of organomercury compounds occurred in Minimata Bay, Japan, in the 1950s. Metallic mercury released from a paper factory on the shores of the bay was methylated in the sediments by bacteria to form methyl mercury. Mercury in its methylated form is much more bioavailable than liquid mercury and it passed rapidly along the food chain until it reached high concentrations in fish.

The local people relied heavily on locally caught fish and were thus exposed to poisoning. About 100 people died and many suffered severe disabilities from mercury poisoning. Such incidents are most severe when a local population is highly dependent on a single food source but are rare in more developed regions where food is obtained from much wider sources. Similar problems are likely to occur in the near future in the Amazon Basin. Huge quantities of mercury are being dumped into the river as a by-product of gold refining, and there is evidence that this is becoming methylated and is passing into food chains.

3.4: Gaseous pollutants

The most important gaseous pollutants are ozone (O₃) and oxides of carbon, nitrogen and sulphur. On a global level, the main concern with ozone is the reduction in its concentration in the upper atmosphere. Ozone 'hole' which occurs over the Antarctic is caused by the effects of chlorofluorocarbons (CFCs) on ozone molecules. The ozone layer absorbs ultraviolet light, so that one hazard associated with its thinning is an increase in the rates of skin cancer. Environmentally, it has been suggested that the increased U.V. radiation could decrease photosynthesis of phytoplankton in the Antarctic. At a local level, ozone is produced in photochemical smog, in which oxides of nitrogen from car exhausts (NO and NO₂, sometimes known as 'NO_x' or 'NOX' gases) and fumes from other fossil fuel consumption react with moisture under the action of sunlight. High concentrations of ozone in the air irritate respiratory epithelia of animals and can directly affect the growth of some plants. Levels of carbon dioxide rarely reach toxic concentrations, except in very confined places. Sulphur dioxide is produced mainly from volcanoes and fossil fuel burning. The SO₂ dissolves

in water droplets, forming sulphurous and sulphuric acids which fall as 'acid rain'. Rain with a low pH may directly damage the leaves and roots of plants. Furthermore, nutrients may be washed out of acidified soils as the hydrogen ions displace essential elements from soil particles. Plants growing on such soils may become deficient in one or more trace elements. Acid rain may also increase the mobility of metal pollutants in soils if the pH drops sufficiently low. The effects of acid rain are much greater on soils and lakes with a low buffering capacity. One of the reasons why Scandinavia has been so badly affected by acid rain is the poor buffering capacity of the soils developed from the granite bedrock which underlies much of the region.

3.5: Radioactive isotopes

Since the development of nuclear energy and atomic weapons, there has been an ongoing debate as to the safety of low levels of radioactivity in the environment. We are all exposed to background radiation from cosmic rays and the natural decay of radioactive isotopes. Some consider that this exposure is beneficial as it promotes natural DNA repair mechanisms. Others consider that there is no safe level of radiation. The contribution of different sources to overall natural background radiation depends to a large extent on local geology. One of the most important sources is radon gas, which may reach levels that give cause for concern in poorly ventilated houses.

3.6: Nano-materials

Nanomaterials are natural and manmade materials having at least one dimension of 100 nm or less. Although nanoparticles can be natural in origin as in the cases of silica and asbestos fibers, the term is most commonly used for manufactured particles. Natural nanoparticle sources include fires and volcanoes. Anthropogenic sources include unintentional ones such as internal combustion engines, smelters, and electric motors. Nanoparticles also include intentionally engineered particles.

Engineered nanomaterials are used in products including electronics, optics, textiles, medical devices, cosmetics, water treatment technologies, fuel cells, catalysts, biosensors, and bioremediation materials. These new materials include single and double-walled carbon nanotubes, metallic, metal oxide, and metal hydroxide.

The same concerns about health effects of asbestos fibers have been expressed for carbon nanotubes. Gold and silver nanoparticles can be a source of dissolved metals and cause oxidative stress. Indeed, one of the major applications of silver nanoparticles is as a bactericide incorporated into various products. Gold nanoparticles are more inert than those of silver. The movement and phase association of nanoparticles after release into the environment depend on their physical and chemical features. The same is true regarding their fate on entering an organism. A human health example is **metal fume fever**, a disease caused by breathing in metal-rich fumes that are produced during smelting, metal casting, and similar activities. Metals inhaled deep into the lungs are released from the metal-rich particles, often zinc oxide, and gain entry to the bloodstream. Metal oxides can have negative surface charges and, as a consequence, can become associated with other ions and coated with natural dissolved organic materials. Physical association with other molecules can influence nanoparticle movement into and their effects on organisms.

3.7: Pathogenic organisms

Pathogenic organisms identified as capable of causing illness when present in water and soil include such microorganisms as viruses, bacteria, protozoan parasites, and blue-green algae, as well as some macroorganisms—the helminths, or worms—which can grow to considerable size.

- **Viruses** are organisms that usually consist only of nucleic acid (which contains the genetic information) surrounded by a protective protein coat. The nucleic acid may be either ribonucleic acid (RNA) or deoxyribonucleic acid (DNA). They are always obligate parasites; as such, they cannot grow outside of the host organism (*i.e.*, bacteria, plants, or animals), but they do not need food for survival. Viruses that infect bacteria are called **bacteriophages** and those bacteriophages that infect intestinal, or coliform, bacteria are known as **coliphages**.
- **Bacteria** are prokaryotic single-celled organisms surrounded by a membrane and cell wall. Bacteria that grow in the human intestinal or gastrointestinal (GI) tract are referred to as **enteric bacteria**. Enteric bacterial pathogens usually cannot survive for prolonged periods of time in the environment.

- **Protozoa** are single-celled animals. Protozoan parasites that live in the GI tract are capable of producing environmentally resistant cysts or oocysts. These oocysts have very thick walls, which make them very resistant to disinfection.
- **Helminths** (literally “worms”) are multicellular animals that parasitize humans. They include roundworms, hookworms, tapeworms, and flukes. These organisms usually have both an intermediate and a final host. Once these parasites enter their final human host, they lay eggs that are excreted in the feces of infected persons and spread by wastewater, soil, or food. These eggs are very resistant to environmental stresses and to disinfection.
- **Blue-green algae**, or **cyanobacteria**, are prokaryotic organisms that do not contain an organized nucleus— unlike the green algae. Cyanobacteria, which may occur as unicellular, colonial, or filamentous organisms, are responsible for algal blooms in lakes and other aquatic environments. Some species produce toxins that may kill domestic animals or cause illness in humans.

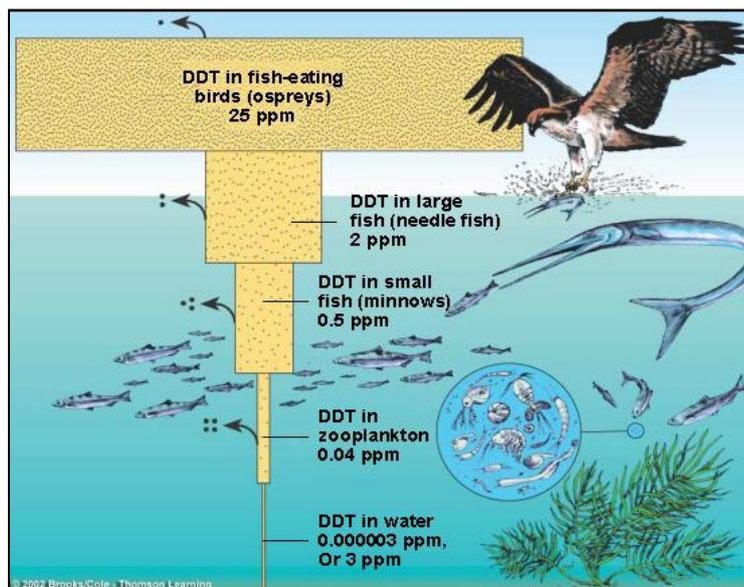
Lecture 2

4. Pollutants properties

4.1. Bioaccumulation of pollutants

One of the important properties of pollutant if it was bioaccumulative. **Bioaccumulation** refers to the accumulation of a toxic chemical in the tissue of a particular organism. **Biomagnification** refers to the increased concentration of a toxic chemical in the food chain. This happens when a microbe, plant, animal, or human is only very slowly able to break down a chemical or if the chemical finds a site within the body that firmly binds it. For example, PCBs are difficult to break down, and being accumulate in fatty tissues. A

chemical undergoing biomagnification reaches gradually higher levels in the fat as it moves through the food web. Some metals bioaccumulate too, but not in fat. Lead concentrates in bones and teeth. Cadmium builds up in the kidneys. Mercury attaches itself to proteins in many locations, especially in the liver. In addition, ecologists used other term (Bioconcentration) which means the



accumulation of freely dissolved contaminant in water by aquatic organisms through non dietary routes. In water-only exposures, the primary route of uptake of dissolved contaminants in fish is across the gill epithelium, but depending on the compound and animal body size. While bioaccumulation means the uptake of a chemical (e.g. pesticide) by a living organism by using all possible routes, for example contact, respiratory surfaces, and ingestion.

4.1.1: Factors impacting bioaccumulation

The degree to which a contaminant accumulates in biota depends on the qualities of the contaminant, the organism, and the environmental conditions under which the organism and contaminant are interacting. The qualities of the contaminant determine the physical and chemical form in which it is present in the environment and the degree to which it is available to be taken up, biotransformed, and eliminated. Physiological and genetic qualities determine an organism's ability to take up the contaminant. Developmental or sex related changes can influence bioaccumulation. For example, age- and sex-correlated lipid content will influence

accumulation of a lipophilic contaminant. Ecological and behavioral characteristics of an organism determine routes of exposure and efficiency of uptake from each potential source. Environmental conditions can also directly modify the functioning of an organism. For example, temperature has a clear influence on rates of the physiological and biochemical processes taking place within the organism. Other factors such as salinity and pH strongly modify ion regulation and osmoregulation and, in so doing, influence the uptake of many contaminants.

4.1.2: The difference between bioaccumulation and biosorption

Bioaccumulation and Biosorption differ when considering the mechanism. In the process of biosorption, pollutants are bound to the surface of cellular wall of the biomass, in bioaccumulation contaminants are transferred into cellular interiors. Biosorption can be performed by non-living biomass, but the essential condition for bioaccumulation to occur is that an organism should be metabolically-active.

The route through which a bioaccumulant enters an organism is usually the same through which it takes up nutrients or food. In unicellular organisms, toxic metals enter through the transport channels, usually wrongly with essential elements (e.g. Ca (II) or Mg(II)). In plants, some toxic metals are transported from water and soil through the root system.

The route of transfer also depends on which environment is the mostly polluted with a given metal: water, soil or air. In animals, the routes through which toxic metals are bioaccumulated are mainly alimentary tract (food and water contaminated with toxic metals), but also from respiratory system (from polluted air) and through skin (contact exposure).

In general the comparison between biosorption and bioaccumulation process listed below

Biosorption	Bioaccumulation
Passive process	Active process

Metals are bound with cellular surface

Adsorption

Reversible process

Biomass is not alive

Nutrients are not required

The rate is quick

Not controlled by metabolism

No danger of toxic effect

Metals are bound with cellular surface and interior

Absorption

Partially reversible process

Biomass is alive

Nutrients are required

The rate is slow

Controlled by metabolism

Danger of toxic effects caused by contaminants

4.1.3: Biomarkers

The principle behind the biomarker approach is the analysis of an organism to their metal contents in order to monitor the metal excess in their tissues. In general biomarker refers to any biological response in a living organism that results from the exposure to a pollutant.

- **Definition**

Classical definition: Biochemical, physiological or histological indicators of either exposure to or effects of, xenobiotic chemicals at the suborganismal or organismal level.

Nato workshop (1993): A biological response that can be related to an exposure to, or toxic effect of, an environmental chemicals.

Depledge (1993): A biochemical, cellular, physiological or behavioural variation that can be measured in tissue or body fluid samples at the level of the whole organism that provides evidence of exposure to or effects of one or more environmental chemicals.

The effects of contaminants at lower levels of biological organization (e.g. biochemical, cellular, physiological) in general occur more rapidly than those at higher levels (e.g., ecological effects) and therefore may provide a more sensitive early warning of toxicological effects within populations. Potentially, any alterations in any of the molecular, cellular, biochemical, and physiological processes occurring within an organism following pollutant exposure could be used as biomarkers. Biomarkers, in general, may be classified into **biomarkers of exposure**, and **biomarkers of effect**.

1. Biomarkers of exposure: covering the detection and measurement of an exogenous substance or its metabolite or the product of an interaction between a xenobiotic agent and some target molecule or cell that is measured in a compartment within an organism; Biomarkers of exposure can be used to confirm and assess the exposure of individuals or populations to a particular substance (group), providing a link between external exposure and internal dosimetry.

2. Biomarkers of effect: including measurable biochemical, physiological or other alterations within tissues or body fluids of an organism that can be recognized as associated with possible health impairment or disease. Biomarkers of effect can be used to document either preclinical alterations or adverse health effects due to external exposure and absorption of a chemical.

4.2: Pollutants move

Although pollutants seldom stay in one place, we often act as if they do. Pollutants move through air, water, and soil, and may contaminate food. Pollutant effects are typically greater near their source, but pollutants often move and may have effects far from their sources too.

4.2.1: Pollution is greatest near the source:

Many pollutants are detected far from the point of emission, and can exert adverse effects at a distance - acid deposition is an example. But the greatest effects typically arise near the emission's source. Dioxins emitted from an incinerator can also travel thousands of miles. But, again the highest fallout occurs near the incinerator.

4.2.2: Pollutants may enter ecosystems

Pollutants may enter ecosystems as the consequence of human activity in the following ways:

1. 'Unintended' release in the course of human activities (e.g. in nuclear accidents, mining operations, and fires);
2. Disposal of wastes (e.g. sewage, industrial effluents);
3. Deliberate application of biocides (e.g. pest control).

Some of the chemicals so released can also reach unusually high levels locally as a result of natural processes such as weathering of rocks (many metals and inorganic anions) and volcanic activity with associated forest fires (SO₂, CO₂ and aromatic hydrocarbons). There

are problems of defining what actually constitutes pollution. Some authorities prefer to restrict the terms ‘pollution’ and ‘pollutants’ to the consequences of human activity.

However, it is sometimes difficult or impossible to determine the relative contribution of human processes and natural ones to residues that are present in the general environment.

4.2.2.1: *Entry into surface waters*

The discharge of sewage into surface waters represents a major source of pollutants globally. Domestic wastes are discharged mainly into sewage systems. Industrial wastes are discharged *either* into the sewage system *or* directly into surface waters. The quality of the sewage that is discharged into surface waters depends on

- (i) the quality of the raw sewage received by the sewage works and
- (ii) the treatment of the sewage that takes place within the works .

The pollutants present in surface waters exist in diverse states. They may be in solution and/ or in suspension. Suspended material may be in the form of droplets (e.g. oil), or particles and pollutants may be dissolved in droplets or absorbed by solid particles. All of these forms can be transported by water over considerable distances. Particulate material is liable to fall to the bottom of surface waters, e.g. where the rivers enter the sea their rate of flow is slow and the transported particles fall to the bottom with estuarine deposits. Liquid droplets may rise to the surface or may be carried down by particles to the sediment, depending on their density.

With oil pollution, both of these things occur— light oil rises to the surface, but ‘heavy’ oil residues go into sediment. In rivers, pollutants are transported over varying distances. The distances travelled depend on factors such as the stability and physical state of the pollutants and the speed of the flow of the river. The distance travelled is likely to be greatest where stable compounds are in solution and where rivers are fast flowing.

The importance of long-distance transport of pollutants by the rivers was clearly demonstrated when the river Rhine became polluted with the insecticide endosulfan in 1969. The initial release was evidently in the middle section of the river, near Frankfurt, but the transported compound was detected by Dutch scientists working near the Rhine estuary some 500 km downstream.

Once pollutants reach lakes or oceans, they may be transported by currents. The major

oceans of the world are traversed by surface currents, so it is possible for pollutants to be moved from one continent to another. These currents are wind driven. In both the Atlantic and the Pacific oceans, there are large circular patterns of currents over most of the surface area. The movement is clockwise in the northern hemisphere, but counterclockwise in the southern hemisphere.

The density of sea water is an important factor. Water may increase in density as the result of a fall in temperature or of an increase in salt concentration (e.g. because of evaporation). When water masses increase in density, they move towards the bottom of the ocean. It is sometimes assumed that oceans are so large that dilution will quickly reduce pollutant concentrations to such low levels that they no longer constitute a problem. The movement of matter with currents, and its subsequent precipitation, ensures unequal distribution. Inshore waters tend to have substantially higher levels of pollution than the open sea. When persistent pollutants enter marine food chains, they can be moved over large distances by migrating animals and birds. Some fish, whales and fish-eating sea birds migrate over thousands of miles, taking pollutants with them. This can lead to transfer from one ecosystem to another, e.g. where contaminated fish or birds migrate over large distances and are then eaten by vertebrate predators.

4.2.2.2: Discharge into the atmosphere

Pollutants enter the atmosphere in the gaseous state, as droplets or particles. When in the gaseous state, they may be transported over considerable distances, with the movements of air masses. Particles and droplets, on the other hand, are more likely to move over only relatively short distances before falling to the ground. However, sometimes undergo long-distance transport when they are of small diameter.

Carbon dioxide (CO₂), sulphur dioxide (SO₂), oxides of nitrogen (NO_x), hydrogen fluoride and chlorofluorocarbons (CFCs) are examples of gases released in this way. The combustion of fuels releases CO₂, SO₂, NO_x and a variety of organic compounds (e.g. PAHs) which are products of incomplete combustion. The level of pollution depends on the quality of the fuel. Some forms of coal (e.g. brown coal) are high in sulphur and can cause very serious pollution with SO₂. The subsequent movement of pollutants is dependent upon atmospheric conditions

and on the height and the form of the smokestack releasing them. Under clear and warm conditions, pollutants will be quickly diluted because of the mixing of air. As the earth's surface is warmed by sunlight, hot air will rise from the vicinity of the smokestack, producing convection currents and carrying pollutants with it. Cold, clean air will flow in to replace it. In the evening, this process may be reversed, as the air cools. Then, if there is no wind, a layer of fog may form, trapping a cold air beneath it. The following morning the sun will be unable to penetrate the layer of fog, thus preventing a warming of the air and consequent dispersal of air pollutants. The air pollutants will become trapped in the vicinity of the smokestack from which they were emitted.

Thus, in general, the dispersal of air pollutants is favored by warm, dry conditions with a steady side wind. The dispersal of pollutant will be more effective from high smokestack than from of release, the greater the height that pollutants will reach in the atmosphere and the greater the distance that they are likely to travel.

The internal-combustion engine represents another important source of air pollution. The engines of aeroplanes and ships cause pollution of air and sea. During the operation of internal-combustion engines, chemical reactions take place which generate substances not originally present in the petrol. Carbon monoxide and nitrogen oxides are released, together with a variety of organic molecules which are the products of incomplete combustion.

Petrol is also a source of organolead and inorganic lead compounds which arise from tetra-alkyl lead, used in some petrols as an 'antiknock' (to control semi-explosive burning during the operation of the engine). Nowadays, there is a strong movement towards the greater use of lead-free petrols to reduce the emissions of lead in its various forms from car exhausts.

The control of emissions from internal-combustion engines is a complex subject that will only be considered in outline here. In an 'uncontrolled' vehicle, effectively all of the carbon monoxide, nitrogen oxides and inorganic lead compounds and about 65% of hydrocarbons are released from the exhaust system.

With modern engines, there have been considerable improvements in design which reduce all these sources of pollution. Exhaust emissions are substantially reduced by the incorporation of catalytic converters and filters into the exhaust system. These remove nitrogen oxides,

carbon monoxide and hydrocarbons. Further improvements in exhaust emission have come through the optimization of engine performance (critical factors are air— fuel ratios, ignition timing and cylinder design).

Air pollution also arises because of the use of pesticides. The application of pesticides as sprays or as dusts is not a very efficient process. A substantial proportion of the pesticide that is applied does not reach the crop or the soil surface. Aerosol droplets, dust particles with adhering pesticides and pesticides in the gaseous state pass into the air. This is a particularly difficult problem when pesticides are applied aurally. Climatic factors influence the extent to which pesticides contaminate the atmosphere. Strong side winds tend to move them away from original areas of application, with the risk that neighboring areas lying downwind will be contaminated. Volatilization is most rapid where air temperatures are highest. Thus, pesticides show a greater tendency to volatilize into the air under tropical conditions than they do under temperate conditions. Another factor of importance is droplet size. Very small spray droplets produced during low volume spraying fall more slowly to the ground than large droplets because their sedimentation velocity is slower and they are liable to travel for relatively long distances before reaching the ground. In general, environmental factors such as wind speed, temperature and humidity need to be taken into account when planning spray operations in order to maximize the amount of pesticide reaching its target and to minimize air pollution.

Radiochemical pollution of the air due to the explosion of atomic devices on or above the land surface was a problem for many years after the last war. By international agreement, however, this practice has now been discontinued, but concern remains over accidental release from establishments such as power stations and atomic research stations which handle nuclear materials. The seriousness of the problem was clearly illustrated by the Chernobyl accident of 1986 in the Ukraine, when a nuclear reactor caught fire with consequent widespread air pollution with radionuclides . Half of the reactor contents were dispersed.

Some air pollutants are in the gaseous state. Examples include CO, NOX, SO₂, HF and small volatile halogenated molecules such as CFCs, trichloroethylene (CCl₂=CHCl) and carbon tetrachloride (CCl₄). These may move through the air by two processes—mass transport and diffusion. Air movements on the global scale are relatively complex. First, there

is a layer of air close to the earth's surface (say up to 4 km in height) which is subject to particular turbulence and localized air flow. Pollutants released within this zone are likely to return to ground quickly, travelling only relatively short distances.

On the other hand, pollutants which reach greater heights may be transported over considerable distances, carried by circulating air masses. The part of the atmosphere relevant to this discussion extends some 35 km above the earth's surface. This is the lower atmosphere, which accounts for about 99% of the total air mass. It is divided into the troposphere (first 10–11 km) and the stratosphere, which lies above it. The troposphere is characterized by strong vertical mixing. There is little vertical mixing in the stratosphere above it. The boundary between these two layers is termed the tropopause. Within the troposphere, there are regular patterns of air circulation, characteristic of different climatic zones. Pollutants may be brought down by rain or may be transferred to land surface by **dry deposition** at distances far removed from their original point of release.

4.2.3: **Pollutants can be buried in sediments**

Sediments are materials deposited at the bottom of a lake, river, or other water body. They mostly contain materials carried to the water in rain. Sediment is composed of soil, minerals, and organic material. When in the water the material settles to the bottom as sediment. Very fine particles may remain suspended for some time rather than settling out; such suspended solids can be very damaging to aquatic life. By its very nature, sediment is buried by additional incoming sedimentary material. Pollutants such as metals or long-lived organic chemicals may be buried in sediments, but cannot be depended upon to remain buried. Bottom-feeding organisms may take the pollutants back up, and reintroduce them into the food chain. Riverine and coastal-area sediments are sometimes dredged, which also brings contaminants back to the surface. Natural water currents such as a strong river flow also move sediment, especially that near the surface.

Lecture 3

4.3: Toxicity of pollutants

The major reason that we care about a pollutant is that it may be toxic -- to ourselves, to wildlife, and to plants. Researchers agree on definitions for bioaccumulation and bioconcentration, but there is not a common definition for toxicity. The type and degree of toxicity varies with each pollutants. For example DDT has low acute toxicity in mammals, but dioxin (2,3,7,8-TCDD) demonstrates extreme acute toxicity for mammals.

4.3.1: Threshold effect

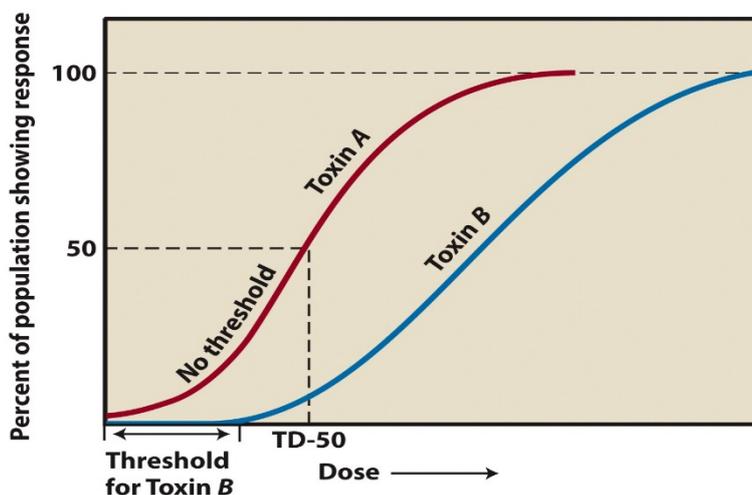
Threshold is a level below which no effect occurs and above which effects begin to occur.

-If a threshold exists, then a concentration below the threshold is safe.

-If there is no threshold dose, then even the smallest amount has some negative toxic effect. A problem in evaluating thresholds for toxic pollutants is that it is difficult to account for synergistic effects.

4.3.2: Acute and chronic toxicity

“Acute toxicity” is an adverse effect seen soon after a short-time exposure to a chemical. An acute effect may be vomiting, diarrhea, irregular heartbeat. In contrast, “chronic toxicity” results from long-term exposure to lower doses of a chemical or occurs after exposure has ended. Long term may be several weeks or more than 30 or 40 years. A well-known chronic effect is cancer, which usually does not develop until long after initial exposure. The typical latency period for cancer (the time of initial exposure to the time that cancer is diagnosed) is 15 to 25 years. Leukemia, a cancer of white blood cells, may result from long-term exposure to benzene. A substance that does not cause acute effects may show chronic toxicity. If you break a mercury thermometer, your one-time exposure to elemental mercury vapor is unlikely to hurt you, but chronic exposure to mercury vapor in a workplace can seriously affect the nervous system. Anything is toxic at a high-enough dose. Even drinking very large quantities



of water has killed people by disrupting the osmotic balance in the body's cells. As the dose of a chemical increases there are many possible toxic effects.

4.3.3: Factors modifying the toxicity of pollutants

Just as there are a large number of pollutants in our environment, so there are many factors that affect the toxicity of these pollutants. The major factors affecting pollutant toxicity include physicochemical properties of pollutants, mode of exposure, time, environmental factors, interaction, biological factors, and nutritional factors.

4.3.3.1: Physicochemical properties of pollutants

Characteristics such as whether a pollutant is solid, liquid, or gas; whether it is soluble in water or lipid; and whether it is organic or inorganic, ionized or nonionized, etc., can affect the ultimate toxicity of the pollutant. For example, since membranes are more permeable to a nonionized than an ionized substance. One of the most important factors affecting pollutant toxicity is the concentration of the pollutant. Even a generally highly toxic substance may not be very harmful to a living organism if its concentrations remain very low. On the other hand, a common pollutant such as carbon monoxide can become extremely dangerous if its concentrations in the environment are high. As mentioned earlier, exposure to high levels of pollutants often results in acute effects, while exposure to low concentrations may result in chronic effects. Once a pollutant gains entry into a living organism and reaches a certain target site, it may exhibit an action. The effect of the pollutant, then, is a function of its concentration at the locus of its action.

4.3.3.2: Time and mode of exposure

Exposure time is another important determinant of toxic effects of pollutants. Normally, one can expect that for the same pollutant, the longer the exposure time the more detrimental the effects. Also, continuous exposure is more adverse than intermittent exposure, with other factors being the same. For example, continuous exposure of rats to ozone for a sufficient period of time may result in pulmonary edema. However, when the animals are exposed to ozone at the same concentration intermittently, no pulmonary edema may be observed. The mode of exposure, i.e., continuous or intermittent, is an important influence on pollutant toxicity because living organisms often can, to a certain degree, repair injuries caused by

environmental agents. In addition, organisms may be able to develop tolerance so that they will be able to withstand otherwise toxic doses of chemical substances.

4.3.3.3:Environmental Factors

Environmental factors such as temperature, light, and humidity also influence the toxicity of pollutants.

In the literatures numerous effects of temperature changes on living organisms have been reported. The rate at which chemical reactions occur increases with increased temperatures. Temperature affects the response of vegetation to air pollution. Generally, plant sensitivity to oxidants increases with increasing temperature up to 30°C. Soybeans are more sensitive to ozone when grown at 28°C than at 20°C, regardless of ozone doses.

Generally, the sensitivity of plants to air pollutants increases as relative humidity increases. However, the relative humidity differential may have to be greater than 20% before differences are shown. MacLean *et al.* (1973) found gladiolus plants to be more sensitive to fluoride as relative humidity increased from 50 to 80%.

4.3.4. Biological factors

4.3.4.1.Species

A chemical that harms one species at a given dose may not be toxic to another. However, toxicity varies greatly by species. Considering how widespread dioxin is in the environment, humans are fortunate to be less sensitive than many other species. Even so, dioxin poses major concerns.

4.3.4.2.Variation within a species

Within a given species, individuals may vary greatly in their sensitivity to a toxicant. Some may be very sensitive, others very resistant. Consider the sulfites (widely used in food preservation). Some humans are hypersensitive to these chemicals, but there is no indication of adverse effects in most people at levels commonly used. The immune system in babies and small children is less well developed than in adults. They often -- but not always -- are more sensitive to toxicants than adults; At the other end of life, the immune system of aged persons may function less well than in younger adults.

4.3.4.3.Nutrition manners :

Good nutrition provides protection against xenobiotics and infectious microorganisms (pathogens). Individuals who consume high-fat foods have a greater risk of colon and skin cancer.

4.3.4.4. Tolerance

The ability to resist or withstand stress resulting from exposure to a pollutant or harmful condition (toxicity). This ability results from behavioral, physiological, or genetic adaptation.

1. Behavioral tolerance- change in behavior or learning to avoid the pollutant toxicity.

2. Physiological tolerance- the body of an individual adjusts to tolerate a higher level of pollutant. Includes many mechanisms including detoxification such as the toxic chemical is converted to a nontoxic form. Or internal transport of the toxin to a part of the body where it is not harmful, such as fat cells.

3. Genetic tolerance- (adaptation) when some individuals in a population are naturally more resistant to a toxin than others. Such as strains of mosquitoes resistant to DDT or antibiotic resistance.

5. Interaction of Pollutants

Seldom are living organisms exposed to a single pollutant. Instead, they are exposed to combinations of pollutants at the same time. In addition, the action of pollutants is dependent on many factors including portals of entry, action mode, metabolism, and others. Exposure to combinations of pollutants will no doubt lead to manifestation of effects different from those that would be expected from exposure to each pollutant separately. The combined effects may be synergistic, potentiative, or antagonistic, depending on the chemicals and the physiological condition of the organism involved.

Usually an animal, person, or plant is exposed to more than one chemical at a time. What is the result of multiple exposures?

— The most common effect is **additive**. This commonly happens when all the chemicals exert their effects in the same manner, as when a person is exposed to several organophosphate pesticides for example at the same time ($1+1+1=3$). Each organophosphate pesticide acts the same way, it inhibits the activity of a specific enzyme. In this case, add up the concentration of each organophosphate pesticide to obtain the total dose.

_ **Synergism** presents the greatest concern. When two chemicals act synergistically their combined effect is greater, sometimes much greater, than additive (1+1 equals more than two.) An instance is lung-cancer risk from radon. The lung-cancer risk is magnified if a person smokes. In another case, researchers administered a low dose mixture of lead, mercury, and arsenic to pregnant mice. They observed greater deformities in the fetuses than would be expected by simply adding up the concentrations of the three metals.

_ **Antagonism** occurs with some chemicals. One chemical interferes with the action of another - it acts as an antidote.

6. Biochemical effects of pollutants

6.1: Introduction

When pollutants enter living organisms, they cause a variety of changes. These changes (bio-effects) are, broadly speaking, of two kinds: those which serve to protect the organisms against the harmful effects of the chemical and those which do not. We consider, first, **protective responses**. Some protective mechanisms work by reducing the concentration of free pollutants in the cell, thereby preventing or limiting interactions with cellular components which may be harmful to the organism. Organic pollutants often cause the induction of enzymes that can metabolize them. One of the most important of these enzyme systems is the monooxygenase system, whose function is to increase the rate of production of water-soluble metabolites and conjugates of low toxicity which can be rapidly excreted. In this case, metabolism causes detoxification. However, in a small, yet important, number of cases, metabolism leads to the production of active metabolites (e.g. of carcinogens or organophosphorous insecticides) that can cause more damage to the cell than the original compounds.

Another mechanism whereby the bioavailability of pollutants is reduced is by binding to another molecule. This can lead to excretion or storage.

The metallothioneins are examples of proteins which can bind metal ions and which become induced when there is exposure to high metal concentrations. There are also inducible proteins which can bind organic pollutants; this mechanism provides the basis of resistance to some drugs by removing them from the cell. In addition to protective mechanisms which control the levels of free pollutants, there are other responses which are concerned with the repair of

damage caused by pollutants. The release of stress proteins falls into this category. When organisms are exposed to chemical or heat shock, stress proteins are released which have the function of repairing cellular damage. Similarly, if pollutants cause damage to DNA, repair mechanisms can come into play. The health of the organism is adversely affected, sometimes so seriously that death will ensue. Here, the biochemical changes are at the site of action and represent the molecular basis of toxicity. The changes caused by pollutants entering living organisms may be specific for a particular type of chemical or they may be non-specific. Similarly, responses to any particular pollutant may be specific to certain groups of organisms or may occur in nearly all organisms. The degree of induction of monooxygenases in response to a particular pollutant shows considerable phylogenetic variation between species. Thus, some inducing agents produce marked responses in mammals, but no responses in fish or in some birds.

6.2: Protective biochemical responses

When the concentration of a xenobiotic or inorganic ion exceeds a certain level in the cell, it may trigger off responses designed to protect the organism against potential toxic effects. Very commonly, this response is an increase in the *quantity* of a protein which can facilitate the removal of the molecule or ion. In the case of lipophilic xenobiotics, a number of enzymes are *induced* which can increase the rate of biotransformation of the molecule to water-soluble and readily excretable metabolites and conjugates. Induction involves an increase in the activity of an enzyme as a consequence of an increase in its cellular concentration produced in response to a chemical.

Prominent among these enzymes are the monooxygenases of the endoplasmic reticulum of vertebrates and invertebrates, which have cytochrome P450 as their catalytic centre. A number of inducible forms exist in the livers of vertebrate animals. Induction involves an increase in both cytochrome P450 and the enzyme activities associated with it. Many lipophilic xenobiotics are both inducers and substrates for this type of cytochrome P450. These enzymes interact particularly with flat (co-planar) molecules, such as polycyclic aromatic hydrocarbons (PAHs), co-planar PCBs and dioxins. Although metabolism by a cytochrome P450 usually causes detoxication, there are exceptions. In particular, induction of a cytochrome P450, can

cause increased activation of carcinogens (e.g. certain PAHs) . When certain metal ions exceed a critical cellular level, another type of protein is induced. Metallothioneins can increase in concentration after exposure to various metals. These are binding proteins, rich in SH groups, which can lower cellular concentrations of metal ions such as Cu^{2+} , Cd^{2+} and Hg^{2+} by sequestering them . The previous responses are concerned with prevention of toxic damage by the simple strategy of removing potentially harmful xenobiotics and ions before they interact to a significant degree with their sites of action.

Lecture 4

7. Systemic and local effects of pollutants

A systemic effect is one occurring at a point distant from where a chemical enters the body. The terms “toxicant” or “poison” most often refer to substances effects within the body after it has been absorbed. However, we need also to be aware of local effects. Local effects are those that occur at a substance’s point of contact with skin, eyes, or lungs. An acid for instance irritates (or has corrosive effects) at the point where it contacts the body -- it shows local effects. A reactive gas such as formaldehyde also has local effects although absorbed into the body it can have systemic effects too. Or, the metal nickel irritates the skin, but after absorption into the body can also exert systemic effects. Some plants have local irritant effects at the point of contact too. The acronym ADME (refer to Absorption, distribution, metabolism, and excretion) may help you to remember what happens to a pollutant with systemic effects as it is absorbed into, moves through, is modified by, and leaves the body. A chemical enters the body through the lungs, the gastrointestinal tract, or the skin. From its point of entry, it may be absorbed (A) into the bloodstream, and distributed (D) throughout the body. It is typically metabolized (M) by the body’s tissues, and finally excreted (E) from the body.

7.1: Absorption (A)

Unless a chemical has a local effect on the skin, mouth, nose, or eyes, it must be absorbed into the body. This ordinarily can happen in three ways. You inhale it into the lungs, ingest it into the digestive tract, or absorb it across the skin. Sometimes a chemical gains entry in non-ordinary ways, for example when it is injected into a vein or under the skin. Some xenobiotics (foreign chemicals) are toxic only by one route of entry whereas others are toxic in two or three ways.

- _ Formaldehyde can act as a carcinogen only if inhaled.
- _ Radon is also primarily a carcinogen by inhalation.
- _ However, arsenic is toxic by all three routes: skin absorption , ingestion, and inhalation.

■ Ingestion

Anything taken into the body by drinking or eating is ingested. Once in the digestive tract, a substance may be absorbed across the wall of the small or large intestine into the

bloodstream. Most absorption occurs through the small intestine. From there a chemical enters blood system that carries it directly to the liver. Because the liver is the first organ a toxicant contacts -- before it has been much diluted by the bloodstream -- the liver receives the highest dose of an ingested toxicant.

■ Inhalation

Unless you deliberately inject a chemical into the body, inhalation is the fastest means by which a toxic substance can enter the body and exert an effect. Think about inhaling a gaseous anesthetic such as ethyl ether. Anesthesia results very rapidly after the inhaled gas passes from the lung's alveoli into the bloodstream. Many other substances can also be inhaled such as metal fumes, or the particulates in smoke, or aerosol droplets from a spray can. Because effects can often occur so rapidly, workplace exposures in enclosed spaces can be especially dangerous.

■ Skin absorption

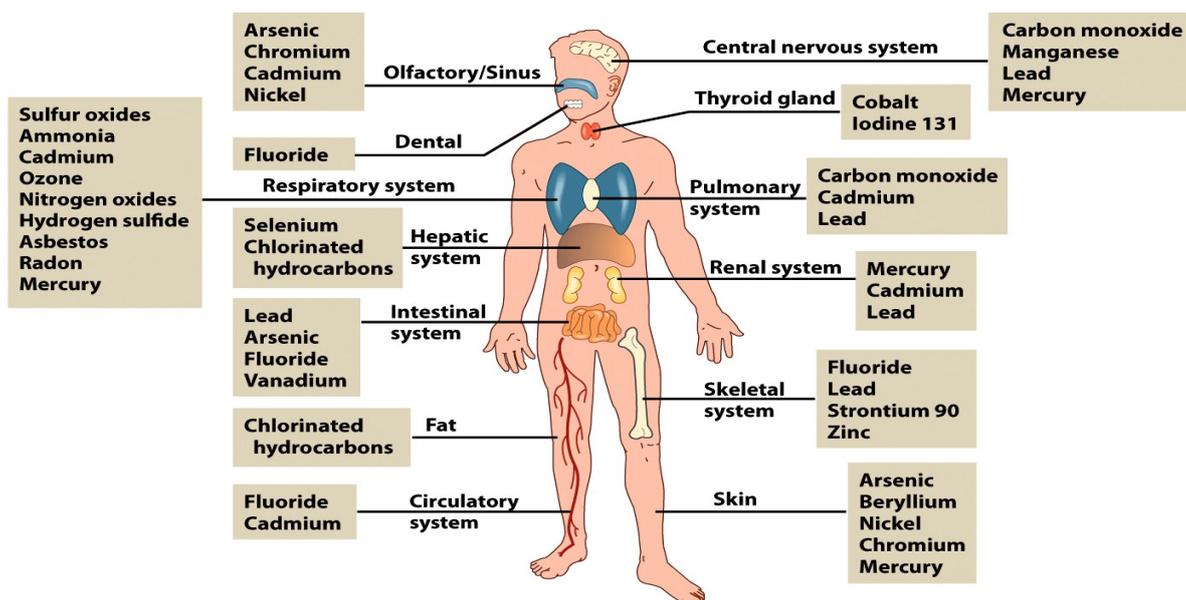
By stopping or slowing the absorption of most chemicals, the skin provides excellent protection from the outside world. Nonetheless some chemicals are absorbed across the skin, sometimes efficiently. The pesticide parathion is one that is absorbed as rapidly through the skin as by ingestion or inhalation. When thinking about skin absorption, remember: Thin skin such as found on the abdomen is more permeable to chemicals than the thicker skin on the hands or feet.

The larger the area of skin exposed to a chemical, the more that is absorbed. The longer a chemical remains in contact with skin, the more that is absorbed. Chemicals such as acids, alkalis, or metals needn't be absorbed to exert effects; their effect is local.

7.2: Distribution (D)

After absorption, a chemical is distributed throughout the body by the blood and is taken up, to varying extents, by different organs. A specific chemical often has a greater effect on one organ than on other organs; this is the organ most sensitive to it, the "target organ". To be toxic, a chemical must reach the most sensitive tissue at a high-enough dose to exert an adverse effect, it is this dose that is important. The nervous system is a major target organ of lead and mercury. However, these metals can affect other organs too as dose increases or time of

exposure increases. Benzene, at high concentrations, causes narcosis due to its impact on the central nervous system. Chronic exposure to lower benzene concentrations can result in anemia or leukemia due to its impact on another target tissue, bone marrow. Often substances are stored in the body; if this happens, they don't usually show toxic effects.



The targets organs by pollutants in human

7.3. Metabolism (M)

To be able to rid their bodies of absorbed pollutants, animals and humans may need to biotransform them into forms that can be excreted. The liver and kidney are especially active in this process.

Usually, the some pollutants is converted into a less toxic chemical. In some time, the result is a more toxic chemical, for example when the liver converts the pollutant benzene into benzene oxide, a reactive chemical; it is benzene oxide that damages bone marrow.

7.3.1: Biotransformation and detoxification

Once a contaminant enters the organism, it becomes available for possible biotransformation. Most biotransformations involve enzymatic catalysis. Biotransformation can lead to enhanced elimination, detoxification, sequestration, redistribution, or activation. It can enhance the rate of loss from the organism as is often the case if a lipophilic xenobiotic is converted to a more reactive or hydrophilic compound, e.g., naphthalene oxidation to naphthalene diol. Some contaminants may be transformed to a form that is retained within the

organisms but is sequestered away from any site of possible adverse effect. With activation, the adverse effect of a contaminant is made even worse by biotransformation or an inactive compound is converted to one with an adverse bioactivity. As an example of activation, the organophosphorus pesticide, parathion,* undergoes oxidative desulfuration to form the very potent paraoxon .

Microbes genetically adapted to metal contaminated environments can have an enhanced ability to add methyl or ethyl groups to a metal ion as in the case of ionic mercury conversion to methylmercury. Regarding organic contaminants can be eliminated rapidly or be subjected to metabolism* with subsequent excretion of metabolites. During biotransformation, lipophilic compounds are often, but not always, made more amenable to excretion by conversion to more hydrophilic products.

Biotransformations of organic contaminants can be separated into Phase I and II reactions. Generally, reactive groups such as $-\text{COOH}$, $-\text{OH}$, $-\text{NH}_2$, or $-\text{SH}$ are added or made available by Phase I reactions, increasing hydrophilicity. One of the most common Phase I reactions involves addition of oxygen to the xenobiotic by a monooxygenase. After formation, the products of Phase I reactions can be eliminated or enter into Phase II reactions. Conjugates are formed by Phase II reactions, which inactivate and foster elimination of the compound. Compounds conjugated with xenobiotics or their biotransformation products include acetate, cysteine, glucuronic acid, sulfate, glycine, glutamine, and glutathione.

7.4.Excretion (E)

After exposure to pollutants, an absorbed pollutants begins to be released. The rate of excretion depends on a number of factors including if and how it has been stored in the body.

_ Water-soluble chemicals are largely excreted in urine. Some chemicals such as salt or sodium cyanide are already water soluble.

_ If a pollutants is not water soluble, the body attempts to biotransform it into a form which is, then excreting it in the urine.

_ Some chemicals cannot be transformed into water-soluble forms. These are excreted with the bile from the liver into the intestine, and exit the body in the feces.

8.The target organs for pollutants

In addition of pollutants can affect any tissue or organ within the body. However, a specific toxicant often has a “target” organ that is more sensitive to its adverse effects.

A few of the organs that toxicants may affect are seen below.

8.1: Liver

This organ carries out many vital functions, one of which is to detoxify pollutants. The liver is the first organ that a pollutants encounters after it is absorbed into the blood from the small intestine ,thus the liver is exposed to higher toxicant levels than organs that the chemical reaches after it has been diluted in the bloodstream. Although the liver usually detoxifies pollutants, sometimes it converts a chemical into a more toxic substance. One example you have already seen is the conversion of benzene, to benzene oxide. The liver is sometimes exposed to larger amounts of a chemical than it can detoxify, as when a person drinks large amounts of an alcoholic beverage. Chemicals that are toxic to the liver (hepatotoxicants) include organic solvents such as chloroform. Ethyl alcohol is a well known hepatotoxicant. Acute toxic effects of excessive alcohol intake are well known. Chronic effects on the liver of excessive alcohol intake include cirrhosis and cancer. Worldwide, perhaps half a million people a year die from liver cancer despite the fact that most should be preventable.

8.2:Kidneys

Like the liver, kidneys can detoxify xenobiotics. However, their major function is to filter the blood, eliminating waste products into the urine while retaining water and nutrients such as glucose. As kidneys filter blood, they concentrate the body’s waste chemicals and foreign chemicals as well. The result is that foreign chemicals can reach higher, even harmful doses. Some pollutants are toxic to the kidneys (nephrotoxicants); so are metals such as mercury, cadmium, and lead.

8.3: Immune system

This complex system of tissues, organs, and cells includes bone marrow, lymph nodes, and spleen. The immune system recognizes the difference between self and what is not self. It rids itself of foreign substances, including microorganisms and cancer cells, using cells that it produces such as lymphocytes and macrophages. A well-functioning immune system also protects individuals against pollutants. Immunotoxic substances are agents that are toxic to the

immune system. They can damage the immune system by suppressing it, or by causing it to overreact. Environmental chemicals such as PCBs, can suppress the immune system. Substances such as tree and flower pollens can cause immune-system over-reactions such as allergies.

8.4: The central nervous system

The brain requires high levels of oxygen to function normally, so any substance that lowers oxygen supply is neurotoxic, i.e., toxic to the nervous system. Carbon monoxide is probably the best-known neurotoxic substance. Some pesticides, including malathion and parathion, nerve gases, and many drugs (legal and illegal), are neurotoxic; so are certain hazardous metals, in particular lead and mercury, and PCBs. Especially in children, neurotoxic effects may be expressed in behavior such as attention deficit disorder. Behavioral problems are intensively studied today as they may prove to be a sensitive way of detecting an adverse effect of a neurotoxic chemical.

8.4.1: Neurotoxic compounds

The nervous system of both vertebrates and invertebrates is very sensitive to the toxic effects of chemicals and there are many examples of neurotoxins—both naturally occurring and manmade. Among the ‘natural’ neurotoxins should be included tetrodotoxin (from the puffer fish), botulinum toxin (from the anaerobic bacterium *Clostridium botulinum*), the natural insecticides nicotine (from the wild tobacco *Nicotiana tabacum* and many more).

Among man-made compounds, it is interesting to note that the four major groups of insecticide—organochlorine, organophosphorous, carbamates and pyrethroid insecticides—all act as nerve poisons.

All of the examples given disturb, in some way, the normal transmission of impulses along nerves and/or across synapses (i.e. junctions between nerves or between nerve endings and muscle and gland cells). However, a distinction can be made between compounds which act directly upon receptors or pores situated in the nerve membrane and those which inhibit the acetylcholinesterase (AChE) of synapses. These two groups will now be considered separately.

The passage of an action potential along a nerve is dependent upon the flow of Na^+ and K^+ across the nerve membrane. During the normal passage of an action potential, Na^+ channels are open for a brief instant, allowing the inward flow of Na^+ ions. They are then closed to terminate the Na^+ flow. Pyrethroid insecticides, natural pyrethrins and DDT all interact with Na^+ channels to disturb this function. The usual consequence of their interaction is retarded closure of the channels. This can cause a prolongation of the flow of Na^+ ions across the membrane, which leads to disturbance of the normal passage of the action potential. This type of poisoning causes uncontrolled repetitive spontaneous discharges along the nerve. It is likely that these compounds first dissolve in the lipids of the nerve membrane before interacting with some site on the Na^+ channel, which spans the membrane.

8.5: Skin

There may be local effects of a chemical on eyes and mucous membranes. An irritant is one of these. Exposed to an irritating chemical, the skin reacts. The irritation subsides when exposure ceases. Many substances may irritate the skin: a weak acid, such as the acetic acid in vinegar, or a detergent or other cleaning product, or the chemicals in certain plants. The skin may redden, swell, or itch. Sunlight is an example of a non-chemical irritant; it can cause reddening, pain, and sensitivity. A serious problem may arise when an irritant is also an allergen. When an allergic person is exposed for the first time to an allergenic chemical the skin reacts and then recovers when exposure ceases just as in a non-allergenic person. However, expose a sensitive person repeatedly, and the reaction grows in severity. Moreover, reactions occur with much lower doses. An allergy has developed. Formaldehyde, a chemical found in many household products, is an irritant, and also an allergen. Some chemicals affect the skin indirectly after having been absorbed into and distributed around the body. Arsenic is a chemical that can have both local and systemic effects on the skin. Systemic effects of arsenic include skin cancer.

8.6:Lungs

Reactive gases such as ozone (found in smog), formaldehyde, ammonia, and chlorine (found in household products) can directly damage the lungs and the mucous membranes in the nose, and can also affect the eyes. Many particles that become airborne can damage the lungs if

breathed in and trapped there. Examples are silica, asbestos, coal or cotton dust. These substances can be inhaled into the lungs, but not completely expelled. Adverse effects can be acute or chronic. Dust inhalation can have an immediate irritant effect, but chronic exposure can damage lung function; cotton dust exposure over many years gives rise to brownlung disease, coal dust to black-lung disease, and silica dust to silicosis.

A number of substances cause lung cancer. These can be solid substances such as asbestos, or a gaseous chemical such as radon. Chemicals in tobacco smoke may be breathed in as either solid particles or gases. Organic solvents evaporate into the air. Breathing too much of the vapor may damage the lungs. Accidental aspiration of a liquid solvent or of gasoline can severely damage lungs or cause death. In other instances, lungs serve as the entry point for chemicals that have adverse systemic effects elsewhere in the body. Volatile organic chemicals evaporated from motor-vehicle products or certain household products are breathed in and enter the bloodstream through the alveoli (tiny air sacs deep within the lungs at the end of the bronchiole tubes). The normal function of alveoli is to provide a surface for an exchange between oxygen and carbon dioxide, but other chemicals can follow the same route.

8.9: Children and the fetus

Almost any toxic effect can pose concerns, but effects on the developing fetus, baby, or tiny child are perhaps our most profound concern. Children represent our future. One public health expert has said, “. . . the weakness of children [is] one of the central public health problems for our time.” One major reason for our concern is that children are often more sensitive than adults to polluted environments. They are often more highly exposed to toxicants than adults.

8.9.1: Why children’s exposure is greater

Children are often more exposed to pollutants or contaminants than adults. They eat more food per pound of body weight. So, if a food is contaminated they ingest more toxicant pound-for-pound. As well as, they also ingest more foods such as fruits that have been treated with pesticides. Children often ingest things that adults typically would not, such as sweet-tasting leaded paint and soil. If the soil is contaminated, they suffer greater exposure.

_ Babies and children breathe more rapidly than adults, thus pound-for-pound they inhale a greater volume of contaminated air. One way in which babies and small children are more

exposed to air pollutants is at home. Children crawl on or play near the floor, and stir up contaminants into the air that they breathe. The small child is also exposed to the metals, such as lead, and other substances in house dust. Carpets are “deep reservoirs” for chemicals, microorganisms, and allergens (animal dander, dust mites, and mold). More generally, indoor air pollution can be much greater than pollution in outside air, especially in wealthy countries where outdoor air pollution is controlled. Indoor pollution may be one cause of the increasing rates of childhood asthma and allergies in urban areas of developed countries, especially as children spend so much time indoors.

Lecture 5

9. Risk assessment for pollutants

How much ozone should we allow in the air we breathe? How much arsenic in drinking water? What level of dioxin in soil or food? These and similar questions arise every day. And, because we seldom have the luxury of answering “zero,” we must determine what level above zero is safe or essentially safe .

- **Risk:** is the possibility of suffering a harm from a hazard that can cause injury, disease, death, economic loss, or environmental damage.

Risk = Hazard × Exposure

- **A hazard:** is the source of the risk -- not the risk itself. For a hazard to pose a risk to you, you must be exposed to it. The word hazard goes beyond chemical hazards: infectious disease organisms, pathogens, are biological hazards; ionizing radiation or hot water are examples of physical hazards.
- **Exposure :**Thousands of industrial chemicals exist. Many are hazardous and could pose a risk. To protect yourself ask first: Am I exposed to it? If so, to what amounts? What is the route of exposure, i.e., does the chemical reach you in air, water, soil, or food?

9.1: Chemical Risk Assessment: Chemical risk assessment is a process that systematically examines the nature and magnitude of a risk. To evaluate the risk, you need to know the inherent toxicity of the chemical to which exposure is occurring, how much exposure is occurring, and other conditions of exposure.

9.1.1: Why do we do chemical risk assessments?

Risk assessment provides answers to questions such as: What is the risk to my child’s health of drinking water containing 3 ppb of atrazine (an herbicide)? What is my risk if I eat meat containing 1 part per billion of benzopyrene (a carcinogen)? What is the risk to a worker who is breathing air containing 1 part per million of benzene (a carcinogen)? How much dioxin (a carcinogen) can safely be left in the soil of a hazardous-waste site when it is cleaned up?

What should be the standard (the limit) for ozone in city air? What should be the standard for arsenic in drinking water? .

The results of chemical risk assessment can be used in more complex situations too. And we can use the results for comparative risk assessment, by comparing one environmental risk to another, for example when we ask, What is the risk of stratospheric-ozone depletion as compared with the risk of acid rain?. Many environmental risks, such as ozone depletion and acid rain, also involve chemicals, so chemical risk assessment is important in comparative risk assessment too. However, comparative risk assessment can take us far beyond the risks of individual chemicals. We can use it to compare the risks of various environmental problems .

_ Another situation where chemical risk assessment is valuable is in analyzing the risks of hazardous-waste sites. However, such sites often have too many chemicals to evaluate each chemical individually. Instead, investigators determine which chemicals are present and in what amounts. Then they do risk assessments on indicator chemicals.

In general, whether we are looking at a hazardous-waste site or a contaminant in air or water, how do we decide when a risk assessment is warranted? First, we must answer the question: Is there exposure to the chemical? If there is no exposure, there is no risk to humans, plants or animals. If there is exposure, then the chemicals of most concern are those that are very toxic or to which we have high exposure.

_ A pesticide's purpose is to kill, and it may harm species other than those it was targeted ; so we do a risk assessment on any new pesticide.

_ Food additives will be ingested, so exposure will definitely occur. A risk assessment is therefore carried out on new additives.

_ There are many chemicals that we already use and are already exposed to, but whose risk has not been systematically studied. More and more people want these chemicals subjected to risk assessments too. Risk assessment is a powerful tool, and the answers it provides are indeed important. Finally , risk assessment is not science; it is a set of decision tools to help us make informed decisions in the absence of definitive scientific information.

Health effects evaluated by chemical risk assessment are in two categories. One is non-cancer health effects; that is, any and all adverse effects other than cancer. The second is cancer. Both cases involve four steps.

9.1.2: Non-cancer risk assessment

There are four steps in the risk assessment of a chemical. First is, why is this chemical considered a hazard? And in dose--response assessment, examines what doses are toxic to laboratory animals. And in third step exposure assessment to the chemical. And in the final step,(risk characterization) takes all the information from steps 1 to 3 for determine the chemical is risk or not.

Step 1. Hazard identification

The first question is how is this chemical hazardous? To do this hazard identification step we collect and analyze information available on the chemical, examining research literature, and other information sources. Just some of the questions needing to be answered follow.

_ What toxic effects does it cause in laboratory animals? Does it, for example, harm the nervous system, interfere with respiration, cause birth defects, or suppress the immune system? How does it affect animals and plants?

_ How does exposure occur: by skin absorption, by ingestion, or by inhalation?.

Step 2. Dose--response assessment

Find a dose safe to laboratory animals. Expose different groups of animals to increasing doses of the chemical. Observe the response to each dose over days, weeks, or months.

_ A control group does not receive the test chemical.

_ A second group receives a low dose. A third group receives a larger dose.

_ A fourth group receives a yet larger dose.

_ The highest dose that animals tolerate without showing ill-effect is the “no observed adverse effect level” (NOAEL). But, what we really want to determine is a dose that is safe to humans exposed to it, even if exposure occurs over a lifetime. So, we divide the NOAEL by a safety factor.

_ Determine a safety factor. To do this, assume the average person is 10 times more sensitive than test animals.

_ Also, assume some humans are 10 times more sensitive than the least-sensitive humans. This means multiplying 10 by 10 to yield a safety factor of 100.

_ If the animal dose--response study is not of high quality, introduce another multiple of 10 to increase the safety factor to 1000. Even if the data are of good quality, consider if children are exposed to the chemical. If they are, increase the safety factor even further .

_ Determine the reference dose. Divide NOAEL by the safety factor. This gives the reference dose (RfD). The reference dose is one considered safe for humans over a lifetime of exposure. The smaller the RfD, the more toxic the chemical.

_ Example: What is the RfD of a chemical with a NOAEL in rats of 1 mg/kg per day (1 milligram per kilogram of animal body weight per day)? Assume that the animal data are good, and divide 1 mg/kg per day by 100. This yields an RfD of 0.01 mg/kg per day. (The RfD is sometimes also called the acceptable daily intake, ADI.)

Step 3. Exposure assessment

What is the human exposure level to the chemical? Wild animals or an entire ecosystem may also be exposed to the chemical, but here we will consider only humans.

_ Source. What are the sources of the chemical? Is it emitted to air or water from an industrial facility? Is it emitted in motor-vehicle exhaust? Is it leaching from a waste dump into groundwater?

_ Route of exposure. How does exposure occur?

_ Is it through drinking water? If so, what is its water concentration, and how much does an average person drink?

_ Is it through food? If so, which foods? What is the concentration in each food, and how much of each is eaten?

_ Is it through soil? If so, what is its concentration in soil, and how much soil is ingested or inhaled (as dust)?

_ Is it through air? If so, what is its concentration in air, and how much is inhaled?

_ In all these cases, for how long does exposure continue?

_ Most highly exposed population.

_ Some Native Americans eat large amounts of fish, and have high exposure to chemicals that concentrate in fish such as PCBs or methylmercury.

_ Children are most likely to ingest soil, and are at special risk from soil contaminants.

- _ Small children living in houses with deteriorated lead paint have high lead exposures.
- _ Urban dwellers may have the highest exposure to motor-vehicle exhaust.
- _ Urban people drinking chlorinated water are most likely to have the highest exposure to disinfection byproducts.
- _ Rural people who drink well water may be more exposed to radon, nitrate, and arsenic.
- _ Individuals living near a hazardous-waste site are more likely to have exposures to chemicals emanating from that site.
- _ Children. Give special consideration to children's exposure.

Step 4. Risk characterization

Risk characterization brings together everything we have learned about the chemical, its hazards, its dose--response toxicity, and exposure to it. This information is used to calculate its risk, its hazard quotient.

- _ If more than one chemical is being evaluated (as when evaluating several chemicals at a hazardous-waste site) the hazard quotients are added together to yield a higher risk.
- _ If there are multiple pathways of exposure to a chemical (food and water for example) these are added together to yield a higher risk.
- _ Remember from dose—response studies that an RfD is the dose considered safe over a lifetime of exposure. So, if a chemical's hazard quotient is less than its RfD, it is not considered a risk.

Lecture 6

Radiation pollution

1. Introduction

One of the most important physical phenomena in our universe is the existence of electromagnetic waves. They consist of electric and magnetic fields rapidly reversing in direction and propagating through space (“radiating”) at a speed of 186,000 miles per second (The speed of light). The number of times per second the direction of the fields go through a cycle (i.e., reverse and then reverse again back to their original direction) is called the frequency, and it determines their behavior and the uses that can be made of them. Frequencies around 1 million cycles/sec are used for radio; television uses about 100 million cycles/sec; radar and microwave ovens use about 10 billion cycles/sec; frequencies around 10 trillion (10^{12}) cycles/sec (are called “infrared”); our eyes sense frequencies of 400-750 trillion cycles/sec, so we call electromagnetic radiation in this range “light”; frequencies of a few quadrillion (10^{15}) cycles/sec are called “ultraviolet”; frequencies above a quintillion (10^{18}) cycles/sec are called “X-rays,” and higher frequencies are known as “gamma rays” .

2. Isotopes

Atoms of the same element can have different numbers of neutrons; the different possible versions of each element are called isotopes. The term isotope is formed from the Greek roots iso (“equal”) and topos (“place”). Therefore: “the same place,” meaning that different isotopes of a single element occupy the same position on the periodic table. The number of protons within the atom's nucleus uniquely identifies an element, but a given element may in principle have any number of neutrons. The number of nucleons (protons and neutrons) in the nucleus, known as the mass number, is not the same for two isotopes of any element. For example, carbon-12, carbon-13 and carbon-14 are three isotopes of the element carbon with mass numbers 12, 13 and 14 respectively. The atomic number of carbon is 6 which means that every carbon atom has 6 protons, so that the neutron numbers of these isotopes are $12 - 6 = 6$, $13 - 6 = 7$ and $14 - 6 = 8$ respectively. Some isotopes are radioactive, and are therefore described as radioisotopes while others have never been observed to undergo radioactive decay and are described as stable isotopes. For example, C14 is a radioactive form of carbon, while C12 and C13 are stable isotopes.

3. Half-Life of a radioisotope

The time for the radiation level to fall (decay) to one-half its initial value. Below some examples of half-life

Radioisotope	Half life
Ra-224	3.6 days
Ra-223	12 days
I-125	60 days
C-14	5700 years
U-235	710 000 000 years

4.The units

4.1. Radiation Activity

Radiation activity is measured in an international unit called a Becquerel (Bq). The Becquerel counts how many particles or photons (in the case of wave radiation) are emitted per second by a source. The device used for measurement is often the familiar Geiger counter. If you put a Geiger counter over a gram of substance and count 3 clicks per second, the radioactivity of that substance would be 3 Becquerel. It is also measured in Curie (Ci), named for Madam Curie, who shared Nobel Prize with her husband. $1 \text{ Curie} = 3.7 \times 10^{10} \text{ Bq}$ or disintegrations per second.

4.2.Absorbed Dose

Absorbed dose describes the amount of radiation absorbed by an object or person (that is, the amount of energy that radioactive sources deposit in materials through which they pass). The units for absorbed dose are gray (Gy) or the radiation absorbed dose (rad). The gray is a large unit and for normal use a series of prefixes are used:

- nanogray (nGy) is one thousand millionth of a gray (1/1,000,000,000)
- microgray (μGy) is one millionth of a gray (1/1,000,000)
- milligray (mGy) is one thousandth of a gray (1/1,000)

Radiation doses are typically given in units of rad- an acronym for radiation absorbed dose by tissue, where 1 rad equals 0.01 joules/kg.

4.3. Equivalent Dose

Dose equivalent (or effective dose) combines the amount of radiation absorbed and the medical effects of that type of radiation. For beta and gamma radiation, the dose equivalent is the same as the absorbed dose. By contrast, the dose equivalent is larger than the absorbed dose for alpha and neutron radiation, because these types of radiation are more damaging to the human body. Units for dose equivalent are the roentgen equivalent man (rem) and sievert (Sv), and biological dose equivalents are commonly measured in 1/1000th of a rem (known as a millirem or mrem). Like the gray, the sievert is a large unit and for normal radiation protection levels a series of prefixes are used:

- nanoSievert (nSv) is one thousand millionth of a Sievert (1/1,000,000,000)
- microSievert (μ Sv) is one millionth of a Sievert (1/1,000,000)
- milliSievert (mSv) is one thousandth of a Sievert (1/1,000)

To determine equivalent dose (Sv), you multiply absorbed dose (Gy) by a radiation quality factor that is unique to the type of radiation. The radiation quality factor takes into account that some kinds of radiation are inherently more dangerous to biological tissue, even if their "energy deposition" levels are the same. For x-rays and gamma rays and electrons absorbed by human tissue, quality factor is 1. For alpha particles it is 20.

5. The sources

Although radiation appears very dangerous, we should remember that individuals are struck by about a million particles of radiation every minute from natural sources.

Table shows the Natural Sources of Radiation

Source	Annual Dose (μSv)
Radon and thoron gas from rocks and soil	800
Gamma rays from ground	400
Carbon and potassium in your body	370
Cosmic rays	300
Total =	1870

One third of this radiation comes from outer space, another third comes from radioactive elements such as uranium, thorium and radium are present in soil, rock, water, and all other environmental media, and certain of these radioisotopes give off gamma rays as they undergo radioactive decay. The principal contributor to the dose from radioisotopes in the body is potassium-40, which decays by emitting an energetic beta particle and gamma rays. The largest contributor is inhalation of radon-220 and radon-222 gases and their short-lived radioactive decay. Ingestion of food and water containing naturally occurring radioisotopes accounts for only a few mrem/yr. In the United States more than 80% of the total dose received by individuals comes from natural sources; 55% comes from radon gas decay products, 8% from cosmic radiation, 8% from terrestrial radiation, and 11% from internal sources such as potassium-40. The rest comes from man-made sources that include medical X-rays (11%), nuclear medicine (4%), consumer products (3%), radioactive fallout, and nuclear power plants (<1%). These percentages are representative, and not all people are exposed to the same sources to the same degree. Below table listed probable annual dose resulting from exposure to man-made sources:

Source	Annual Dose (μSv)
Medical uses – x-rays, etc.	250
Chernobyl (first year)	50
Fall-out from weapons testing	10
Job (average)	5
Nuclear industry (e.g. waste)	2
Others (TV, aeroplane trips, etc.)	11
Total =	328

6. Ionizing radiation

6.1: What is it?

Radiation capable for producing ions when interacting with matter – in other words enough energy to remove an electron from an atom. When one of these particles passes close to an atom, and if there is enough energy in the this particles, this shaking is strong enough to knock the electron loose from the atom. Only the highest frequency particles, X-rays and gamma rays, have enough energy to completely separate an electron from an atom. Since the orbiting electrons are responsible for binding atoms together to form molecules, knocking an electron can destroy a molecule. For example, the water molecule is composed of atoms of hydrogen and oxygen, so an X-ray or gamma ray passing near it can break the molecule up into separate hydrogen and oxygen atoms. Non-ionizing radiation, such as that emitted by a laser, is different because it does not create ions when it interacts with matter.

The three main types of ionizing radiation are alpha particles, beta particles, and gamma rays.

An alpha particle consists of two protons and two neutrons and is identical to the nucleus of a helium atom. Because of its relatively large mass and charge, an alpha particle produces ions in a very localized area. An alpha particle loses some of its energy each time it produces an ion (its positive charge pulls electrons away from atoms in its path), finally acquiring two electrons from an atom at the end of its path. An alpha particle has a short range (several centimeters) in air and cannot penetrate the outer layer of skin.

While beta radiation is small electrically charged particles similar to electrons (Negatrons) with charge of -1 emitted from nuclei of radioactive atoms. Negatrons are identical to electrons and originate in the nucleus of an atom that undergoes radioactive decay by changing a neutron into a proton. The only difference between a negative beta particle (negatron) and an electron is the ancestry. A beta particle originates in the nucleus whereas an electron is external to the nucleus. Beta particles are smaller and more penetrating than alpha particles, but their range in tissue is still quite limited. When its energy is spent, a negatron attaches itself to an atom and becomes an ordinary electron.

Gamma rays are electromagnetic radiation given off by an atom as a means of releasing excess energy. They are bundles (quanta) of energy that have no charge or mass and can travel long distances through air (up to several hundred meters), body tissue, and other materials. A gamma ray can pass through a body without hitting anything, or it may hit an atom and give that atom all or part of its energy. This normally knocks an electron out of the atom, ionizing it. This electron then uses the energy it receives from the gamma ray to create additional ions by knocking electrons out of other atoms.

Additional forms of ionizing radiation include X-rays which are photons (electromagnetic radiations) emitted from electron orbits, such as when an excited orbital electron "falls" back to a lower energy orbit, while gamma rays are photons emitted from the nucleus, often as part of radioactive decay.

6.2: What happens to it in the body?

Radioactive materials can enter the body by inhalation, ingestion, or dermal absorption.

In addition, gamma radiation external to the body can penetrate the skin and produce a dose in various tissues. Inhalation is the primary exposure way for gaseous radioisotopes (such as radon). Ingestion is the primary uptake way for radioisotope in soil, water, and food, including those naturally occurring (such as radium and uranium in soil and groundwater) and man-made (such as plutonium from radioactive fallout).

A fractional amount of ingested radioisotope is absorbed from the gastrointestinal tract into the blood while the rest left the body through normal biological processes with urine and feces. As with inhalation, the extent of uptake depends on the radionuclide and its chemical form. The skin is generally an effective barrier against absorption of radioisotopes, so dermal absorption is a very minor route of exposure.

In general, biological effects of ionizing radiation in the body will depend on several factors.

- 1.Dose: Amount of radiation deposited (or absorbed) in the body.
- 2.Dose rate: Length of time the dose was received.
- 3.Type of radiation: What is the specific type of radiation involved?. Different types of radiation may result in different radiation doses to different parts of the body. Radiation dose exposure may be internal and/or external.
- 4.Organ sensitivity: Some parts of the body, such as the eyes, are more radiosensitive than other parts, such as the hands.

If we are all being struck by a million particles of radiation every minute (expected), why don't we all develop cancer at an early age? . This is returned to this level of radiation is 'safe.' Even a single particle of radiation can cause cancer, but the probability for it to do so is very small, about one chance in 30 quadrillion (i.e., 30 million billion). Therefore, the million particles that strike us each minute have only one chance in 30 billion of causing a cancer. A human lifespan is about 30 million minutes; thus, all of the natural radiation to which we are exposed has one chance in 1000 (30 million/30 billion) of causing a cancer.

6.2.1:Acute and chronic radiation

Potential biological effects depend on how much and how fast a radiation dose is received. Radiation doses can be grouped into two categories, acute and chronic dose.

- **Acute dose**

An acute radiation dose is defined as a large dose (10 rad or greater, to the whole body) provided during a short period of time (few days at the most). If large enough, it may result in effects which are observable within a period of hours to weeks. Acute doses can cause a pattern of clearly symptoms (syndromes). These conditions are referred to in general as Acute Radiation Syndrome. Radiation sickness symptoms are apparent following acute doses ≥ 100 rad. Acute whole body doses of ≥ 450 rad may result in a statistical expectation that 50% of the population exposed will die within 60 days without medical attention. Below are abbreviations for some symptoms during acute exposure:-

1. Blood-forming organ (Bone marrow) symptoms (>100 rad) is characterized by damage to cells that divide at the most rapidly (such as bone marrow, the spleen and lymphatic tissue). Symptoms include internal bleeding, fatigue, bacterial infections, and fever.

2. Gastrointestinal tract symptoms (>1000 rad) is characterized by damage to cells that divide less rapidly (such as the linings of the stomach and intestines). Symptoms include vomiting, diarrhea, dehydration, electrolytic imbalance, loss of digestion ability, bleeding ulcers, and the symptoms of blood-forming organ syndrome.

3. Central nervous system symptoms (>5000 rad) is characterized by damage to cells that do not reproduce such as nerve cells. Symptoms include confusion, convulsions, shock, and the symptoms of the blood forming organ and gastrointestinal tract syndromes. Scientists now have evidence that death under these conditions is not caused by actual radiation damage to the nervous system, but rather from complications caused by internal bleeding, and fluid and pressure build-up on the brain .

Other effects from an acute dose include : 50 rad to the thyroid gland can result in nonmalignant (non cancerous) tumors , 125 to 200 rad to the ovaries can result in permanent

damage in about fifty percent (50%) of women, 200 to 300 rad to the skin can result in the reddening of the skin (erythema), similar to a mild sunburn and may result in hair loss due to damage to hair follicles and 600 rad to the ovaries or testicles can result in permanent sterilization. As a group, the effects caused by acute doses are called **deterministic**. Broadly speaking, this means that severity of the effect is determined by the amount of dose received. Deterministic effects usually have some threshold level - below which, the effect will probably not occur, but above which the effect is expected. When the dose is above the threshold, the severity of the effect increases as the dose increases.

- **Chronic dose**

Chronic dose is a relatively small amount of radiation received over a long period of time. The body is better prepared to tolerate a chronic dose than an acute dose. The body has time to repair damage. The body also has time to replace dead or non-functioning cells with new, healthy cells. The biological effects of high levels of radiation exposure are fairly well known, but the effects of low levels of radiation are more difficult to determine because the deterministic effects described above do not occur at these levels. The main health concern associated with radiation exposure is the induction of various cancers. Additional effects may include genetic mutations and teratogenic effects. Genetic effects are inherited effects which may be expressed in future generations descending from the person exposed to the radiation. Ionizing radiation may induce mutations in the DNA structure that may be expressed in gene mutations. Teratogenic effects on the embryo/ fetus occur as a result of prenatal radiation exposure. The developing human embryo is extremely sensitive to ionizing radiation because cells are rapidly dividing (an embryo of less than 6 weeks is most sensitive and encounters prenatal death as a result of radiation exposure). During the fetal period (more than six weeks) cells become more radioresistant than embryonic cells.

Lecture 7

6.2.2: General effect of radiation on cells

Biological effect arises with the ionization of atoms. The mechanism by which radiation causes damage to human tissue, or any other material, is by ionization of atoms in the material.

Ionizing radiation absorbed by human tissue has enough energy to remove electrons from the atoms that make up molecules of the tissue. When the electron that was shared by the two atoms to form a molecular bond is removed by ionizing radiation, the bond is broken and thus, the molecule falls apart. This is a basic model for understanding radiation damage. When ionizing radiation interacts with cells, it may or may not strike a critical part of the cell. We consider the chromosomes to be the most critical part of the cell since they contain the genetic information and instructions required for the cell to perform its function and to make copies of itself for reproduction purposes. Also, there are very effective repair mechanisms at work constantly which repair cellular damage - including chromosome damage.

The following are possible effects of radiation on cells:

○ **Cells are undamaged by the dose**

Ionization may form chemically active substances which in some cases alter the structure of the cells. These alterations may be the same as those changes that occur naturally in the cell and may have no negative effect.

○ **Cells are damaged, repair the damage and operate normally**

Some ionizing events produce substances not normally found in the cell. These can lead to a breakdown of the cell structure and its components. Cells can repair the damage if it is limited. Even damage to the chromosomes is usually repaired. Many thousands of chromosome aberrations (changes) occur constantly in our bodies. We have effective mechanisms to repair these changes.

○ **Cells are damaged, repair the damage and operate abnormally**

If a damaged cell needs to perform a function before it has had time to repair itself, it will either be unable to perform the repair function or perform the function incorrectly or incompletely. The result may be cells that cannot perform their normal functions or that now

are damaging to other cells. These altered cells may be unable to reproduce themselves or may reproduce at an uncontrolled rate. Such cells can be the underlying causes of cancers.

- **Cells die as a result of the damage**

If a cell is extensively damaged by radiation, or damaged in such a way that reproduction is affected, the cell may die. Radiation damage to cells may depend on how sensitive the cells are to radiation.

Also, some human cells are more sensitive to radiation than others.

- ✓ **Most Sensitive:**

The cells that are rapidly dividing and are the most sensitive to radiation. Examples include mature lymphocytes, erythroblasts and spermatogonia. These cells may be killed or damaged by radiation.

- ✓ **Least Sensitive:**

Cells resistant to the effects of radiation are mature and differentiated. These mature cells may be killed by the radiation or lose their cellular function. Examples of resistant cell types include, nerve cells, muscle cells, red blood cells, and fibrocytes.

7. Depleted uranium

7.1: What is depleted uranium?

Depleted uranium is created as a byproduct during the processing of natural uranium to make it suitable for use as fuel in nuclear power plants or as a component in nuclear weapons. In natural uranium, 99.27% of the mass consists of atoms of uranium-238. About 0.72% of the mass consists of atoms of uranium-235, and a very small amount (0.0055% by mass) is uranium-234. Although uranium-235 is the very rare, it is the one that most readily undergoes nuclear fission and is thus the most useful for common nuclear applications. For most of these applications, the proportion of the uranium-235 isotope found in natural uranium must be increased through a process called enrichment. The uranium enrichment process results in the production of “enriched” uranium (containing >0.72% uranium-235) and “depleted” uranium (containing <0.72% uranium-235). The uranium enrichment process also removes much of the

uranium-234 from the depleted uranium. Most depleted uranium in the United States contains between 0.2 and 0.4% uranium-235, with the remainder being uranium-238 and a slight amount of uranium-234. Depleted uranium is less radioactive than natural uranium because some of the uranium-235 and most of the uranium-234 have been removed.

7.2:How is it used?

Although the vast majority of depleted uranium is stored as a by-product of the enrichment process, several current and potential uses exist. Because of its high density, depleted uranium is currently used for radiation shielding. Military applications of depleted uranium include use as tank armor, tank projectiles (antitank weapons), and in missiles and high-performance aircraft. In a potential future use, depleted uranium could be mixed with highly enriched uranium from retired nuclear weapons to produce nuclear reactor fuel.

Weapon testing shows that when a depleted uranium round penetrates an armored vehicle, it may pass completely through the vehicle and fragment inside the vehicle. Metal fragments from the penetrator and the vehicle's hull can scatter inside the vehicle, killing and injuring personnel, destroying equipment, and causing secondary explosions and fires. As much as 70% of a depleted uranium penetrator can be aerosolized when it strikes a tank. Aerosols containing uranium oxides may contaminate the area downwind. Uranium metal and oxide fragments may also contaminate the soil around the struck vehicle. Tests of depleted uranium penetrators striking depleted uranium armored vehicles have shown that most of the contamination will occur within 5 to 7 meters of the vehicle.

7.3:What happens to it in the body?

Soldiers can be exposed to depleted uranium when intact rounds are in storage or uploaded in armored vehicles, or on the battlefield following the use of depleted uranium munitions. Uranium and its decay products are primarily alpha emitters, emitting only very low levels of gamma radiation. On the battlefield, exposure to depleted uranium can occur several ways. After impact with an armored vehicle, depleted uranium in the form of oxide and metal fragments will contaminate the struck vehicle and the surrounding area, especially if an explosion or fire occurs. After it is ingested, most uranium is excreted from the body within a few days. The small fraction that is absorbed into the bloodstream (0.2 to 5%) is deposited

specially in bone and kidneys. Most of what goes to the kidneys leaves within a few days (in urine), while that deposited in bone can remain for many years. After inhalation, generally only a small fraction penetrates to the lung's alveolar region, where it can remain for years and can also enter the bloodstream.

Uranium is a health hazard only if it is taken into the body. The major health concern is kidney damage caused by the chemical toxicity of soluble uranium compounds; these effects can be reversible depending on the level of exposure. A second concern is for uranium deposited in bone, which can lead to bone cancer as a result of the ionizing radiation associated with the radioactive decay products. Uranium has caused reproductive problems in laboratory animals and developmental problems in young animals, but it is not known if these problems exist for humans.

Lecture 8

Metals pollution

1.Introduction

A metal is defined by chemists as being an element which has a characteristic lustrous appearance, is a good conductor of electricity and generally enters chemical reactions as

positive ions or cations. Although metals are usually considered as pollutants, it is important to recognize that they are natural substances.

However, in most cases, metals become pollutants where human activity, mainly through mining and smelting, releases them from the rocks in which they were deposited during volcanic activity or subsequent erosion and relocates them into situations where they can cause environmental damage.

The extent to which human activity contributes to global cycles of metals can be described by the anthropogenic enrichment factor (AEF) (cadmium 89%, lead 97, zinc 72, manganese 12, mercury 66). From this, it is clear that human activity is responsible for the majority of the global movement of cadmium, lead, zinc and mercury but is relatively unimportant in the cycling of manganese. The AEF for lead is due mostly to the widespread use and subsequent release of lead based additives to petrol.

✓ *Metals are non-biodegradable.*

Unlike some organic pesticides, metals cannot be broken down into less harmful components. Detoxification by organisms consists of ‘hiding’ active metal ions within a protein such as metallothionein or depositing them in an insoluble form in intracellular granules for long-term storage or excretion in the faeces . In addition to carbon, hydrogen, oxygen and nitrogen, all animals need the seven major mineral elements calcium, phosphorus, potassium, magnesium, sodium, chlorine and sulphur for ionic balance and as integral parts of amino acids, nucleic acids and structural compounds. Other metals so called ‘trace elements’ are definitely required, namely iron, iodine, copper, manganese, zinc, cobalt, molybdenum, selenium, chromium, nickel, vanadium, silicon and arsenic. Zinc, for example, is an essential component of at least 150 enzymes, copper is essential for the normal function of cytochrome oxidase and iron is part of haemoglobin, the oxygen-carrying pigment in red blood cells. Boron is required exclusively by plants.

2: Heavy metals

The term “heavy metals” refers to any metallic element that has a relatively high density and is toxic or poisonous even at low concentration. “Heavy metals” is a general collective term, which applies to the group of metals and metalloids with atomic density greater than 4

g/cm^3 , or 5 times or more, greater than water. Pollution caused by heavy metals is now a worldwide phenomenon. Among the many heavy metals, lead (Pb), mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), zinc (Zn), and copper (Cu) are of most concern, although the last three metals are essential nutrients in animal and human nutrition.

These metals enter the environment wherever they are produced, used, and ultimately discarded. Heavy metals are very toxic because, as ions or in compound forms, they are soluble in water and may be readily absorbed into living organisms. After absorption, these metals can bind to vital cellular components such as structural proteins, enzymes, and nucleic acids, and interfere with their functioning. In humans, some of these metals, even in small amounts, can cause severe physiological and health effects.

From the point of view of environmental pollution, in general metals, may be broadly classified in to the following three categories:

1. *Non toxic but accessible*
2. *Toxic but non accessible*
3. *Toxic and accessible*

It is third category of potentially toxic and relatively accessible metals that have attracted more attention from the points of view of environmental pollution. Although the toxic heavy metals are present in the earth crust in trace levels, anthropogenic activities disperse them into the environment, thus adding up to their natural background levels.

2.1: The sources

Heavy metals are naturally occurring elements and can be found deep in the earth crust to natural erosion processes like weathering and abrasion of rocks, soils and sediments by wind and water, a small but significant fraction of natural metals are continuously being mobilized and transported in the environment. Volcanic eruptions, forest fires and aerosol formation above seas also contribute to the natural transport of metals. These processes cause cycling of metals in the environment, resulting in natural background levels in the air, surface waters and soil . There are three main for anthropogenic sources of heavy metal pollution; industry, agricultural use and sewage sludge.

A common sources of heavy metals include electroplating, plastics manufacturing, fertilizer producing factories.

Significant quantities may be added by metal-contaminated wastewater runoff derived from sources including atmospherically deposited metals, residues from pesticide usage, and phosphate detergents, particularly from the metal-processing industry . Growing attention is being given to health hazards presented by the existence of heavy metals in the environment; their accumulation in living tissues throughout food chain, poses a serious health problem.

2.2: The effects

Although some heavy metals are essential trace elements, most can be, at high concentrations, toxic to all forms of life, including microbes, humans and animals.

Together with essential nutrients, plants and animals also take up small amounts of contaminant heavy metal compounds and can concentrate them. As certain heavy metals such as lead, cadmium and mercury have been recognized to be potentially toxic within specific limiting values, a considerable potential hazard exists for human nutrition. Not all the traces of heavy metals in plants and animals are the results of human activity. Some arise through the absorption processes of naturally occurring soil components. Theoretically, every 1000 kg of "normal" soil contains 200 g chromium, 80 g nickel, 16 g lead, 0.5 g mercury and 0.2 g cadmium! Therefore it is not always easy to assign a definite cause for an increased heavy metal content. Even foodstuffs produced in completely unpolluted areas are not entirely free of heavy metals. *Examples for the effects from exposure to the some toxic heavy-metals are listed below:*

1. Lead

Lead can trigger both acute and chronic symptoms of poisoning. Acute toxicity only occur through the consumption of relatively large single doses of soluble lead salts. Chronic toxicity can arise through the regular consumption of foodstuffs only slightly contaminated with lead. Lead is a typical cumulative poison. The danger of chronic toxicity is the greater problem. Basically, as a result of their comparatively high affinity for proteins, the lead ions form bond with the hemoglobin (red blood pigment) and the plasma protein of the blood. This leads to inhibition of the synthesis of red blood cells and thus of the vital transport of oxygen. If the

bonding capacity here is exceeded, lead passes into the bone-marrow, liver and kidneys. Such an intoxication leads to:

- Encephalopathy in the central nervous system (CNS);
- Disturbances in kidney and liver functions progressing as far as necrosis;
- Damage to the reproductive organs;
- Anemia and many metabolic deficiency symptoms.

2. Cadmium

Cadmium is concentrated particularly in the kidneys, the liver, the blood forming organs and the lungs. It most frequently results in kidney damage and metabolic anomalies caused by enzyme inhibitions. It is now known that the Itai-itai sickness in Japan (with bone damage) is a result of the regular consumption of highly contaminated rice. Cadmium, like lead, is a cumulative poison, i.e. the danger lies primarily in the regular consumption of foodstuffs with low contamination.

3. Mercury

Mercury in the form of its methyl compounds is specifically the most toxic of the heavy metals. When consumed orally, it first passes into the liver, the kidneys and the brain. Accumulation only takes place temporarily. A large part is excreted with the faeces. The salts of mercury, in the case of chronic consumption, first cause tiredness, loss of appetite and weight loss. In the end the kidneys fail. As well as damage to brain function, DNA and chromosomal damage, allergic reactions resulting in skin rashes, negative reproductive effects such as sperm damage and birth defects. The methyl-mercury from animal foodstuffs also damages the central nervous system and the immune system. Teratogenic effects have also been observed.

4. Chromium

Chromium (III) is an essential nutrient for humans and shortage may cause heart conditions, disruptions of metabolisms and diabetes. Chromium(VI) is dangerous to human health, mainly for people who work in steel and textile industry and people who smoke tobacco also have a higher chance for exposure to chromium. It can cause the following symptoms

1. Allergic reactions, such as skin rash
2. After breathing it, chromium(VI) can cause nose irritations and nosebleeds
3. Upset stomachs and ulcers
4. Respiratory problems
5. Weakened immune system
6. Kidney and liver damage
7. Alteration of genetic material
8. Lung cancer

Lecture 9

Pesticides pollution

1. Introduction

Pesticides are substances used to prevent, destroy and mitigate any pest ranging from insects, animals and weeds to lower organisms such as fungi, molds, bacteria and viruses. The purposes of pesticide use are to increase the production of food and to promote public health.

2. Insecticide categories

There are many types of pests, and, many types of pesticides developed to fight them. Only three well-known insecticide categories are mentioned here.

2.1. Polychlorinated insecticides

DDT is the best-known organochlorine pesticide. It exerts its toxic effect by acting on nerve membranes to prevent normal conduction of nervous impulses. Lindane, aldrin, and heptachlor are other polychlorinated insecticides also once widely used. Like DDT, most polychlorinated pesticides have been banned, or their use greatly restricted in developed countries because of their environmental persistence, damage to animal populations, and ability to bioaccumulate in animal fat. Other defining characteristics of organochlorine pesticides are low solubility in water and high solubility in lipid materials, including animal fat -- where they bioaccumulate. Fortunately, they have low water solubility, and cling to soil particles. Thus, they have little tendency to dissolve in rainwater and migrate into water bodies or groundwater.

2.2. Organophosphate insecticides

Organophosphates are also toxic to the nervous system of insects, inhibiting the action of the enzyme that breaks down the neurotransmitter acetylcholine; as acetylcholine levels build up. Organophosphates are more acutely toxic than organochlorine pesticides, sometimes much more so. Whereas DDT, for example, has an LD50 of 113 mg/kg in rats, the LD50 of the organophosphate insecticide parathion is 3.6 mg/kg in male rats. Some organophosphate pesticides -- again consider parathion -- are absorbed across the skin, greatly increasing the danger to pesticide applicators. Most acute, human pesticide poisonings are caused by organophosphate pesticides. In fact, these insecticides are chemical relatives of the exceedingly toxic organophosphate nerve gases. Despite their toxicity, organophosphates were more attractive than organochlorines because they have much shorter lives in the environment and, as they are not fat soluble, they don't bioaccumulate to high levels in fat. However, this implies increased water solubility; thus, after application to a field, rainwater can carry the

organophosphates into water bodies or they can percolate down into groundwater. Organophosphate insecticides include diazinon, dimethoate, , malathion, methyl parathion, and ethyl parathion.

2.3. Carbamate insecticides

A few carbamates are exceptionally toxic, but most are less acutely toxic than the organophosphate pesticides. They exert toxicity in a manner similar to organophosphates, but their effects last for a shorter time. Like the organophosphates, they are short-lived in the environment. Because of their lower toxicity, they are often found in products used by homeowners but are less useful to farmers. The carbamate compounds include carbaryl, carbofuran, and oxamyl.

3. Pesticides as pollutants

Almost all pesticides can become pollutants because of the way they are applied, often by aerial spraying . Unfortunately, in most cases, pesticide contamination is a concern.

Herbicides and insecticides are applied over large areas of agricultural fields and forests. Most surface water pesticide contamination results from runoff from lands to which pesticides have been applied. One study of waters in the Mississippi River basin detected more than 40 pesticides.

3.1: What are the potential health effects of pesticides?

Although pesticides are intended to harm only the target pest, if not used correctly, they can also harm people or the environment. The presence of a pesticide in the environment is not necessarily a problem, but it may be a source of exposure. As with all toxic substances, whether the exposure causes harm depends on the dose, how someone is exposed, how sensitive an individual may be to that toxin, and the toxicity of the pesticide involved. Like other chemicals, some pesticides are more toxic than others. A small quantity of a highly toxic pesticide can cause great harm, but almost any substance can cause harm in large enough doses. That's why, when we consider risk, we consider both the toxicity and your exposure to it (how, how much, how long). With most (but not all) pesticides, the more a person is exposed to a particular substance, the greater the chance of harm. The degree of harm depends on the chemical, the situation, and the person. The same is true of pesticides. Very small amounts of even the most

toxic materials may do no or small harm. Less toxic materials in large amounts can cause great harm.

3.2:How are people exposed to pesticides?

People can be exposed to pesticides in three ways:

1. Breathing (inhalation exposure).
2. Getting it into the mouth or digestive tract (ingestion).
3. Contact with the skin or eyes (skin exposure).

Pesticides can enter the body by any one or all three of these routes. Inhalation exposure can happen if you breathe air containing pesticide as a vapor, as an aerosol, or on small particles like dust. Ingestion exposure happens when you eat food or drink water containing pesticides. Skin exposure happens when your skin is exposed to pesticides. This can cause irritation or burns(local effects). In more serious cases, your skin can absorb the pesticide into the body(systemic effects), causing other health effects. Some pesticides evaporate more easily than others so they are more likely to be inhaled. Some break down quickly on surfaces; others last longer.

3.3:Acute Toxicity and Acute Effects

Acute toxicity of a pesticide refers to the chemical's ability to cause injury to a person or animal from a single exposure, generally of short duration. The harmful effects that occur from a single exposure by any route of entry are termed "acute effects." The four routes of exposure are dermal (skin), inhalation (lungs), oral (mouth), and the eyes. Acute toxicity is determined by examining the dermal toxicity, inhalation toxicity, and oral toxicity of test animals. In addition, eye and skin irritation are also examined. Acute toxicity is measured as the amount or concentration of a toxicant—the a.i.—required to kill 50 percent of the animals in a test population. This measure is usually expressed as the LD50 (lethal dose 50) or the LC50 (lethal concentration 50). Additionally, the LD50 and LC50 values are based on a single dosage and are recorded in milligrams of pesticide per kilogram of body weight (mg/kg) of the test animal or in parts per million (ppm). The lower the LD50 or LC50 value of a pesticide product, the

greater its toxicity to humans and animals. Pesticides with a high LD50 are the least toxic to humans if used according to the directions on the product label.

3.4:Chronic Toxicity and Chronic Effects

The chronic toxicity of a pesticide is determined by subjecting test animals to long-term exposure to the active ingredient. Any harmful effects that occur from small doses repeated over a period of time are termed “chronic effects.” Suspected chronic effects from exposure to certain pesticides include birth defects, toxicity to a fetus, production of non-malignant or malignant tumors, genetic changes, nerve disorders, endocrine disruption, and reproduction effects. The chronic toxicity of a pesticide is more difficult than acute toxicity to determine through laboratory analysis.

3.5:Symptoms of Pesticide Poisoning

The symptoms of pesticide poisoning can range from a mild skin irritation to coma or even death. Different classes or families of chemicals cause different types of symptoms. Individuals also vary in their sensitivity to different levels of these chemicals. Some people may show no reaction to an exposure that may cause severe illness in others. Because of potential health concerns, pesticide users must recognize the common signs and symptoms of pesticide poisoning. Inflammation of the skin, is accepted as the most commonly reported local effect associated with pesticide exposure. Symptoms of inflammation of the skin range from reddening of the skin to rashes and/or blisters. Some individuals tend to cough, or sneeze when exposed to pesticide sprays. Other individuals react to the strong odor and irritating effects of pesticide products. One symptom is that the eyes, mucous membranes of the nose, and even the sensitive linings of the mouth and back of the throat feel scratchy. This symptom usually subsides within a few minutes after a person is removed from the exposure to the irritant. However, a reaction to a pesticide product that causes someone not only to sneeze and cough but also to develop severe acute respiratory symptoms is more likely to be a true hypersensitivity or allergic reaction. Symptoms of a true allergic reaction range from reddening and itching of the eyes and skin to respiratory discomfort often resembling an asthmatic condition. Systemic effects are quite different from local effects. They often occur away from the original point of contact as a result of the pesticide being absorbed into and

distributed throughout the body. Systemic effects often include nausea, vomiting, fatigue, headache, and intestinal disorders. In advanced poisoning cases, the individual may experience changes in heart rate, difficulty breathing, convulsions, and coma, which could lead to death.

3.6:Harmful Effects of Some Pesticide Families

1.Fungicides

The acute toxicity of fungicides to humans is generally considered to be low, but fungicides can be irritating to the skin and eyes. Inhalation of spray mist or dust from these pesticides may cause throat irritation, sneezing, and coughing. Chronic exposures to lower concentrations of fungicides can cause adverse health effects. Most cases of human fungicide poisonings have been from consumption of seed.

2.Herbicides

In general, herbicides have a low acute toxicity to humans because the physiology of plants is so different than that of humans. However, there are exceptions; many can be dermal irritants since they are often strong acids, amines, esters, and phenols. Inhalation of spray mist may cause coughing and a burning sensation in the nasal passages. Prolonged inhalation sometimes causes dizziness. Ingestion will usually cause vomiting, a burning sensation in the stomach and diarrhea.

3.Insecticides

Insecticides cause the greatest number of pesticide poisonings in the world. The most serious pesticide poisonings usually result from acute exposure to organophosphate and carbamate insecticides. Organophosphates and carbamates inhibit the enzyme cholinesterase, causing a disruption of the nervous system. All life forms with cholinesterase in their nervous system, such as insects, fish, birds, humans, and other mammals, can be poisoned by these chemicals.

3.7:Effects on non-target species

When the pesticides used the target pests and those around them such as birds, other animals, and beneficial insects are also more highly exposed, and often suffer adverse effects or die.

-Birds. Cornell University has estimated that in the United States alone, at least 67 million birds die each year from pesticide poisoning. Birds die as a direct result from pesticide exposure or from eating pesticide-treated seeds, or insects; or if they are raptors through eating

poisoned prey. On the US east coast, the deaths of as many as 2 million birds in one incident were associated with carbofuran, an insecticide, which is also extremely toxic to humans.

- Fish. Fish have died by the thousands or, in some cases by the millions, along with other aquatic species. Deaths are attributed to pesticide runoff or to pesticide drift settling onto water.

- Amphibians. An alarming trend is the disappearance, or reduced populations worldwide, of frogs and other amphibians. Amphibians have thin skins making them especially weak to pesticides.

3.8: Pest resistance

Resistance is a major pesticide-use problem. One or more individuals in the target population of insects, plants, or other pests may have a genetic mutation that permits them to tolerate the pesticide. When the resistant individuals reproduce, they pass resistance genes to their offspring. Over time, the resistant population increases until few individuals susceptible to the pesticide are left. Often, when applicators meet resistance they respond by applying larger quantities of pesticide. This allows the pest to express resistance to the higher doses too. Because some pest species reproduce very quickly and in huge numbers, resistance can sometimes develop rapidly. Insect resistance has appeared in as little as 5 years in some instances. About 535 insect and mite species, 210 weed species and 210 plant diseases now resist one or more pesticides. These numbers are growing and some weeds resist all known pesticides. Insects have inhabited Earth for several hundred million years, plants and microbes for much longer still. They have adapted to ever-changing sometimes dramatically different conditions. Man-made chemicals are but one more challenge. Consider the *Anopheles* mosquito that carries the malaria parasite. Worldwide, 2.4 billion people live in locales where they could contract malaria, which causes about 3 million deaths a year. DDT and other pesticides once killed *Anopheles* mosquitoes easily, and the possibility seemed real that malaria could be wiped out. Now, the mosquitoes are increasingly resistant; and in some places the incidence of malaria is higher than before pesticides were introduced. The process of pests developing resistance to pesticides is entirely analogous to microorganisms developing resistance to antibiotic drugs.

3.8.2: Cross- resistance

Consider now the development of resistance by a pest species to an insecticide used to control it; this has often been due to the emergence of a genetically distinct strain of the pest that possesses a target site that is insensitive to the insecticide. Now, as we have seen, many insecticides belong to families whose members share the same mode of action. Thus, there is a strong probability that *resistance* due to a mutant gene that encodes for an atypical form of a site of action will extend to different members of the same group of compounds, regardless of whether they have been exposed to the insecticide. In other words, we may expect to find *cross-resistance*.

The appearance of cross-resistance due to the appearance of a mutant gene that encodes for an insensitive form of the target site of an insecticide is a common phenomenon. Cross-resistance has often been found when comparing individual members of the same group of insecticides that share the same mode of action. It can also be found between members of different classes of insecticide if they share the same mode of action. An example of this is shown by some strains of housefly to DDT. This type of resistance is due to one or more mutant forms of a sodium channel found in the nervous system. Both DDT and pyrethroid insecticides act upon this site—and strains resistant in this way to DDT also show cross-resistance to pyrethroids .

3.8.3: Resistance as an indicator of pollution

Earlier in this text examples were given of the development of resistance by insects to insecticides that was characterized by the emergence of resistant strains of pest species. Resistance genes were identified that encoded for insensitive target sites or an increased activity of detoxifying enzymes. A striking case of this was the development of resistance to pyrethroids by strains of the tobacco bud worm in cotton crops in the southern United States. A similar situation apparently exists in the case of plants that develop tolerance to copper and other metals in old mining areas.

In both of these scenarios exposure to a pollutant led to a change in the genetic composition of a population. So, in principle, identifying certain types of genetic change at the population

level should be a way of detecting environmental effects of pollutants. It has potential as a means of environmental monitoring. An example of it is given by Parker and Callaghan (1997). They studied the exposure of blackfly larvae (*Simulium equinum*) in English rivers to low levels of OPs. There was evidence for an elevation of esterase levels in fly populations that had been subject to exposure to OPs over a period of time.

An interesting example of resistance was found in a nonmigratory estuarine fish inhabiting New Bedford Harbor, in USA, an area polluted by polychlorinated biphenyls (PCBs) since the 1940s . These fish were found to have a high level of resistance to PCB.

Lecture 10

Water pollutants

1.Introduction

Water makes up 60% of a cell and is vital for survival of life. More than 70% of earth's surface is covered with water. It is largely found in oceans and other large water bodies. Water

is continuously recycled through the process of evaporation and transpiration, precipitation, run off, etc.

2. Point and non point sources

A “point source” is “any single certain source . . . from which pollutants are discharged, e.g., a pipe, ship, or factory smokestack.” Outlet pipes of industrial facilities or wastewater-treatment plants are examples of point sources. Point sources originate in large easily identified facilities and thus are easy to trace. Developed countries control most point sources well.

B: Nonpoint source (NPS) pollution, unlike pollution from industrial and sewage treatment plants, comes from many diffuse sources. NPS pollution is caused by rainfall or snowmelt moving over and through the ground. As the runoff moves, it carries away natural and human-made pollutants, finally depositing them into lakes, rivers, wetlands, coastal waters, and even our underground sources of drinking water. Atmospheric depositions are also sources of nonpoint source pollution.

3. Class of water pollutants

Pollutants regulated by the US Clean Water Act are described here. These are the “conventional,” “non-conventional,” and “toxic” pollutants.

3.1: Conventional pollutants

“conventional water pollutants” does correctly involve that these are common pollutants produced in large amounts. These conventional pollutants are as follows: biochemical oxygen demand, nutrients, pH, suspended solids, oil and grease, and pathogenic microorganisms.

3.1.1: Biochemical oxygen demand

Microorganisms decompose organic matter discharged to a water body. They require oxygen to do so. The amount of oxygen required to decompose a given amount of organic pollutant is the “biochemical oxygen demand” (BOD). Natural BOD, such as plant debris and wildlife feces, is almost always present. However, a high BOD often indicates human activity, such as sewage or industrial discharge. Human activities that lead to a discharge of BOD include municipal waste water treatment plants, food-processing operations, chemical plants, pulp and paper operations.

A high BOD can reduce or deplete the oxygen in water. In a large water body, fish can swim away from low-oxygen (“hypoxic”) conditions, but crabs and snails and sedentary organisms may die. Sciences has noted, “Low oxygen now causes more mass fish deaths than any other single agent, including oil spills, and it ranks as a leading threat to commercial fisheries and the marine environment in general.

3.1.2: Nutrients

A nutrient is a substance required for life, but has a more threatening at high concentrations. Man-made fertilizers, containing concentrated reactive nitrogen and phosphorus are a major source of nutrients to water bodies. When fertilizer is added to agricultural fields, the excess runs off with rainwater into water bodies. Human activities that lead to the discharge of organic matter include municipal wastewater-treatment plants, food-processing operations, and chemical plants. Natural sources of nutrients likewise are similar to those noted for BOD, i.e., plant and animal debris and wildlife feces. Continuing input of excess nutrients can lead to eutrophication, a process “during which a lake or estuary evolves into a bog or marsh and eventually disappears.” A water body naturally becomes eutrophic, but over many years as it slowly accumulates nutrients. During later stages of eutrophication, the water is choked with plant life, in particular algal “blooms.” Blooms may form a scum on the water surface, produce offensive smells, give the water a bad taste, and make it unfit for swimming. Human activities that put excess amounts of nutrients into water accelerate eutrophication. Nitrate and ammonia, as well as many organic chemicals, contain nitrogen in a form bioavailable to plants and algae. Excess nutrients – the “nitrogen glut” -- have become a global problem.

3.1.3: Suspended solids

This physical pollutant is found naturally in water to varying extents. As usual, it is an excess that is deleterious. Fine particles in soil runoff become fine suspended solids in water, which can cause serious problems. Increased suspended solids content makes water more turbid or

cloudy. This limits the sunlight reaching aquatic plants and stunts their growth. Fine suspended solids can also clog fish gills and harm the respiration of other water animals.

Suspended solids can interfere with efficient water disinfection by shielding microorganisms from the disinfectant. A major source of suspended solids is soil runoff from agricultural fields, especially in row crops. Forestry and construction activities contribute too.

3.1.4: Oil

Oil spills are a major problem in some near-coastal waters, killing or adversely affecting fish, other aquatic organisms, birds, and mammals. These spills can also kill or reduce organisms living in coastal sands and rocks, and may kill the worms and insects that are food to birds and wildlife. When the spills intrude into coastal marshes, the oil can damage or kill fish, birds, and other animals. Despite the sometimes horrendous damage caused by oil spills, they are seen as a relatively minor problem for fish and the marine environment in comparison to chronic nutrient pollution. Spills are not the only source of oil in water: oil leaking from vehicles, or released during accidents, washes off roads with rainwater and then reaches water bodies. Used oil from motor vehicles is often improperly disposed of too. Direct releases of oil into water bodies also occur.

3.1.5: Pathogenic microorganisms

Most microorganisms are not pathogens, and do not cause disease. Most perform useful, often vital, functions for humans including assisting the digestion in our intestines. We depend on microbes to degrade organic wastes in the environment and to biodegrade the organic material in landfills. We use microbes in fermentations to make food products. Microbes are almost everywhere in our environment, found almost anywhere that one looks. Pathogens that are capable of causing infectious disease, that concern us. A pathogen can be a bacterium, virus, fungus, protozoan, or toxic algal species.

Pathogens in drinking water are a great health threat. Other threats posed by pathogens follow.

_ If infectious microbes or their toxins are found in shellfish

_ Pathogenic viruses and bacteria in coastal water can infect swimmers and others. Viruses are abundant in marine waters, often surviving in salt water longer than bacteria. Infections

can result not just by ingesting water containing pathogens, but through the skin. In the United States, as many as 19 out of 1000 swimmers each year are reported to suffer gastroenteritis caused by swimming in water containing infectious microbes.

Pathogenic microbes in a water body are often anthropogenic, generated by human activities.

_ **Runoff.** They may arrive in water bodies in runoff of storm water, and from operating septic systems, or runoff from livestock operations.

_ **Point sources.** Pathogens sometimes come from point sources, especially poorly performing municipal sewage-treatment plants.

_ All these sources exist in developed countries. The situation is worse in less-developed nations where most sewage remains untreated, and is often dumped into rivers and oceans.

3.2: Toxic pollutants

A specific pollutant, such as lead or chloroform, often contaminates more than one environmental medium, you won't be surprised to learn that many common air pollutants are common water pollutants too. Recall too that hazardous air pollutants (HAPs) are often called toxic air pollutants. The US EPA, under the Clean Water Act, regulates 126 toxic pollutants including metals such as arsenic, cadmium, lead, mercury, nickel, copper, and zinc. Among the toxic pollutants that are organic chemicals, are the widely used industrial chemicals such as benzene, toluene, and many pesticides. Many of these too are HAPs.

A high concentration of toxic water pollutant such as a pesticide may cause acute illnesses or death in aquatic life. In the United States, hundreds of fish kills are still reported each year that result from runoff of spilled pesticides or other chemicals. In smaller quantities, many toxic pollutants present a chronic health risk, e.g., some pesticides may act as environmental hormones. If the toxic pollutant comes from a point source, e.g., a wastewater-treatment facility, it can usually be well controlled. Control is more difficult for toxic pollutants found in non-point-source runoff, as with pesticides from agricultural fields, organic chemicals in runoff from city streets, or polycyclic aromatic hydrocarbons (PAHs) deposited from air.

3.3: Non-conventional and non-toxic pollutants

A third group of water pollutants regulated under the Clean Water Act is the non-conventional and non-toxic pollutants. Here we find ammonia, chloride (as from sodium chloride, salt), iron, aluminum, total phenols, and color. Many facilities -- textile factories are an example -- discharge colored effluents. Thermal pollution can cause problems but is not ordinarily as serious as many other pollutants discussed in this lecture.

4.Impact of pollution on water bodies

When thinking about the impact of a pollutant, be sure to consider the type of water body involved: a river, lake, stream, wetland, estuary or coastal water, ocean, or groundwater.

_ A given quantity of pollutant running off at one time into a large fast-running river may have minimum impact, but the same amount may damage a slow-moving stream or small lake. Of course, if the pollutant continues to enter the large river, it too may be damaged. Or a river may carry continuing inputs of pollutants to locales where they do cause damage -- as happens with the dead zones described below. Metals are natural components of sea water, and a one-time small additional input may go unseen. But, adding the same amount to a fresh-water lake, where metal concentrations are normally low, may cause problems.

Lakes also may have little exchange of water to dilute the metal. Of course sea water too, especially coastal water, may be badly polluted by continuing input.

_ If you add an organic pollutant to surface water, microbes may break it down, assisted by oxygen, sunlight, and wave movement, or it may evaporate. Conversely, groundwater has fewer means to degrade these pollutants, and hence their impact is more severe.

4.1:Coastal pollution

“Everything we do on land ends up in the ocean.” About 80% of coastal and estuary pollution arises from rainwater, and atmospheric deposition. Both these deposit a great variety of pollutants, often great quantities as well. Historically, oceans seemed infinitely able to accept anything that we dumped into them. They diluted and dispersed pollution of all kinds. But as human population grew, especially coastal population, and human activities grew too, coastal waters became increasingly unable to deal with massive pollutant inputs. Fisheries and other coastal resources important to humans have degraded. Wildlife and bird populations have decreased due to ongoing destruction of habitat by development, but also due to pollution.

Worldwide about two billion people, a third of humanity, lives within a hundred kilometers of a coastline.

Nutrients have become a major coastal-water pollutant. Consider the results of an 8-year study. It reported that coastal inputs of reactive nitrogen had increased in North America, and Europe. You need only recall, “the dose makes the poison,” to think that such sharp increases may have adverse effects. Fertilizer runoff is the major source of this reactive nitrogen (as nitrate) pollution, both from upstream runoff into rivers and coastal activity. Air deposition of nitrate is also important; it too can come from afar. Sewage nutrients are a third source.

4.2:Groundwater pollution

Groundwater is a vital resource on which more than one-quarter of the world’s population depends for drinking water. When groundwater is very deep, runoff contaminants may not reach it. However, much groundwater used for drinking is in shallow aquifers. Moreover, there is close connection between shallow groundwater and surface water, so groundwater pollution can pollute adjacent surface water. Compare an organic pollutant in groundwater to one in surface water. Groundwater has fewer microbes to digest organic pollutants, less oxygen, no sunlight, and no surface from which organic pollutants can evaporate. Especially in slow moving groundwater, pollutants may persist indefinitely. Organic chemicals, such as certain oils that have low water solubility pose special problems. Trapped in soil and rock below and around the groundwater, they continue to slowly leach into water maintaining contamination indefinitely. Metals of course don’t degrade, but may become tightly bound to the soil. Surface pollutants, dissolved in water, percolate down through the soil. Shallow groundwater, that closest to the surface is most easily contaminated. How much pollutant reaches groundwater depends on soil type, pollutant characteristics, and the distance to groundwater.

5:The “nitrogen glut”

The “nitrogen glut” is described as “one of the world’s biggest environmental problems.” This phenomenon considered very common now. You also understand the adverse effects of acid deposition with its ability to increase environmental levels of sulfur and nitrogen (reactive

nitrogen). Actually, acid deposition contributes to the nitrogen glut although the biggest source of reactive nitrogen is runoff. Humans have doubled the rate at which reactive nitrogen is reaching plant life.

5.1: Background of the nitrogen glut

Atmospheric nitrogen is biologically inert to most living organisms. Until the twentieth century, people fertilized their crops by applying compost (decaying leaves, grass, and other organic materials). Or they periodically planted their fields with legumes; these have root nodules that contain nitrogen-fixing bacteria, and so increase reactive nitrogen in the soil. This process fixed atmospheric nitrogen into ammonia. Ammonia can be used directly as a fertilizer or converted into nitrate used in fertilizer mixtures that also commonly contain phosphorus and potassium. Synthetic fertilizer has received credit for allowing humanity to increase food production to keep pace with population increases in the twentieth century. Over half of all synthetic fertilizer used in human history was used in the last 20 years of the twentieth century. The amount of synthetic fertilizer now used each year has come to equal the amount of naturally available reactive nitrogen, and its use is growing.

Fertilizer use is projected to increase about 70% by 2020. This is especially so in Asian, African, and South American countries, which now use relatively little. The amount of nitrate reaching coastal areas is directly related to the amount that runs off, so as fertilizer use increases, the amount of nitrate that rivers carry into coastal zones could more than double by 2050 compared with 1990 levels. Burning fossil fuels is a secondary, but important, source of reactive nitrogen. Nitrogen oxide (NO_x) emissions worldwide quintupled in the twentieth century so that NO_x now represents about one-quarter of the reactive nitrogen that humans produce. However, unlike reactive nitrogen from fertilizer, NO_x cannot be trapped in buffer zones: it is deposited directly from the atmosphere after conversion to nitrate or nitric acid. Poorly treated or untreated sewage is a nutrient source too; so is runoff of animal manure. Any organic matter has nutrient value, so any excess amount of such matter reaching water bodies contributes to reactive nitrogen increases in water. Natural sources of reactive nitrogen also exist. Bacteria produce the largest natural amount; of most interest here is reactive nitrogen produced by bacteria in the root nodules of certain plants, especially legumes.

5.2: Adverse effects of excess nutrients

Reactive nitrogen is already a critical problem in some places, and is fast becoming a planet-wide problem. Excess nutrients change the composition of life forms starting at the bottom of the food chain. This change moves through the food web to affect plant, bird, and animal diversity. Excess reactive nitrogen can also result in algal blooms and “dead zones” (described below). Reactive nitrogen is emphasized here, but phosphorus can also cause major harm, especially in freshwater bodies.

1. Algal blooms

Excess nitrate and phosphorus from fertilizers, atmospheric deposition of nitrate, plus nutrients in sewage and manure are associated with eutrophication. In coastal areas nitrate is the major culprit whereas in fresh water lakes, it is more often phosphorus.

_ Any algal bloom can have ill-effects: by crowding out the growth of other plants and covering the water surface so thickly that sunlight is prevented from reaching underwater grasses. These grasses provide food, shelter, and a spawning ground for crabs, fish, and other aquatic creatures as well as habitat for their offspring, and food for water fowl.

_ A bloom can create aesthetic problems too, i.e., unpleasant smells. A bloom also exerts BOD as it is degraded by oxygen-requiring bacteria, sometimes leaving the water hypoxic.

_ Harmful algal blooms (HABs), in addition to the problems just noted, also produce toxins. The bloom of one dinoflagellate, appears as a red tide in marine coastal water. Red-tide organisms produce a toxin that accumulates in the fish and organisms that eat them. The fish may become ill and suffer impaired reproduction and damaged immune systems. Humans eating the contaminated fish may suffer from paralytic fish poisoning. The occurrence of a red tide is one reason for placing a ban on eating fish in an affected area. Water birds and other sea life may also suffer ill-effects.

2. Dead zones

A water body or a portion of a water body where oxygen has been depleted is called a dead zone. Several examples of dead zones follow. The Black Sea is an almost landlocked body of water in Eastern Europe bordered by Bulgaria, the Republic of Georgia, Romania, Russia,

Turkey, and Ukraine. Activities in these and 15 other countries upstream on the Danube River, badly polluted the Black Sea with fertilizers, untreated human sewage, and industrial waste. Year-round severe eutrophication and hypoxia developed, and the incidence of red-tide blooms greatly increased. A final blow came in the early 1980s when an exotic (foreign) species, the Atlantic jelly comb was accidentally released into the Black Sea. This jelly fish bloomed so wildly that it became the dominant Black Sea species. It destroyed native fish species, and 20 of the 26 commercial fish species became extinct. Finally, the jelly fish almost wiped out the zooplankton on which they themselves fed, leading to the end of their population. Countries bordering the Black Sea finally developed a plan to reduce nutrient inputs and encourage treatment of human sewage. A major change occurred after 1990. The Soviet Union had supported agriculture including chemical fertilizer use. After its government collapsed, fertilizer use fell by more than half. In 1996, after more than 30 years, the dead zone disappeared.

Beginning in the late 1970s, Denmark's, which links the North and Baltic Seas suffered algal blooms, low-oxygen water, and fish kills. A plan was developed to cut nutrient input to the strait, phosphorus by 80% and nitrate by 50%. Farmers were to limit application of fertilizer to their fields. When, by 1998 nitrate inputs still had not decreased, the government bought land from farmers to establish wetlands and forests to soak up nitrate, and also paid farmers to use less fertilizer. The phosphorus effort was more successful. Industry and wastewater-treatment plants successfully reduced phosphorus in their effluents, and over a 14-year period the desired 80% reduction in phosphorus was achieved. Because algal blooms in part of the affected coastal area are limited by the amount of phosphorus available, conditions improved with, e.g., oxygen levels rising in the strait's open waters.

In the US Gulf of Mexico, a dead zone -- which at its largest was equivalent in size to the state of New Jersey -- occurs each summer in bottom waters near the mouths of the Mississippi River. The Gulf of Mexico drains water from 31 states, representing about two-thirds of the water of the continental United States, starting in Minnesota and including every state. The gulf receives massive doses of nutrients. An estimated 16% of all nitrate fertilizer applied to crops in the Mississippi River watershed runs off and is delivered to the gulf.

This reactive nitrogen is estimated to account for two-thirds of the nutrient problem. Additional nutrient inputs come from runoff of manure at confined-animal feeding operations and point-source pollution from municipal wastewater-treatment plants. Studies of gulf sediment showed that nitrate and phosphorus levels had increased since 1960. The excessive nutrients stimulate algal blooms in the gulf leading to hypoxic water. As oxygen becomes increasingly scarce, fish move elsewhere. A 31-state plan has developed proposing to pay farmers to reduce fertilizer use, restore wetlands, plant tree or grass buffers between crops and streams, reduce manure runoff, and assist municipal sewage-treatment plants to upgrade their equipment enabling them to remove more nitrate and phosphorus.

Lecture 11

New trends for reducing pollution

1.Green chemistry

An ideal chemical reactions should have a number of attributes such as:

- 1.Safety
- 2.Simplicity
- 3.Selectivity
- 4.High yields
5. Energy efficiency
- 6.Use recyclable raw materials and reagents
7. Absence of hazardous byproducts or at least minimizing them.

In practice, it is imposible to achieve all these attributes. Indeed it is a challenge for chemists and engineers to identify environmentally better reaction pathways that optimize the balance of all the desirable attributes.

Green chemistry is the application of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products .

1.1:The principles of green chemistry

Chemical developments also bring new environmental problems and harmful unexpected side effects, which result in the need for ‘greener’ chemical products. A famous example is the pesticide DDT.

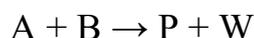
The green chemistry program supports the invention of more environmentally friendly chemical processes which reduce or even eliminate the generation of hazardous substances. This program works very closely with the twelve principles of Green Chemistry. The 12 principles are:

1. It is better to prevent waste than to treat or clean up waste after it is formed.
2. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. Avoid hazardous materials (reagents, starting materials and solvents).
4. Chemical products should be designed to preserve efficiency of function while reducing toxicity.

5. The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible and harmless when used.
6. Recognize energy costs and minimize them
7. A raw material should be renewable rather than depleting wherever technically and economically practicable.
8. Reduce byproducts
9. Catalytic reagents (as selective as possible) are higher to persistence reagents.
10. Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into harmless degradation products.
11. Analytical methods need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
12. Whenever possible choose substances that minimize physical danger (explosions, fires, etc.).

1.2: Green chemistry in applications

In approaches to generic cases, If the reaction is of the type:



Where A and B are feeds, P is the desired product and W a waste by-product

- Find alternate A and/or B feeds to avoid or decrease the amount of W
- Find alternate A and/or B feeds to create a different W, which is a useful by-product
- Find substitute for P that does not entail the co-production of W.

Example: Disinfection of water by chlorination. Chlorine oxidizes the pathogens thereby killing them but at once forms harmful chlorinated compounds. A remedy is to use another oxidant, such as ozone.

▪ Green chemistry for pesticides

Two major goals of “green chemistry” are to develop chemicals that are less toxic or to make them in less toxic ways, if possible both. The development of pheromones and growth regulators are examples of green chemistry. These are toxic only to the insect which we need to kill them. Other examples can achieve the green chemistry criteria too:

_ A herbicide (applied at only teaspoons per acre) affects only a plant enzyme, and has very low toxicity to humans and animals.

_ An insecticide (also only applied in tiny quantities) affects an insect enzyme, and shows low toxicity to non-target species.

_ One herbicide approved by the EPA for use on corn and soybeans has an LD50 in rats of greater than 500 mg/kg body weight; that is, it is only slightly toxic. Moreover, the herbicide is not a teratogen or carcinogen, breaks down quickly in the environment, and does not threaten groundwater.

2.Environmental impact assessment (EIA)

An environmental impact assessment (EIA) is an assessment of the possible positive or negative impact that a proposed project may have on the environment. EIA is widely accepted as a tool in environmental management for reducing pollution.

2.1:Purpose

EIA is intended to identify the impacts (both beneficial and adverse) of a proposed public and private development activities. Often, the focus is dominantly environmental (biophysical); but good practice also addresses social and economic aspects. EIA is mainly used at the level of specific developments and projects such as dams, industrial plants, transport infrastructure (eg airport runways and roads), natural resource exploitation. EIA is most valuable when applied early in the planning process for a project as a support to decision-making. It provides a means to identify the most environmentally suitable option at an early stage, the best practicable environmental option, and alternatives to the proposed projects; and thus avoid or minimize potentially damaging and costly negative impacts, and maximize positive impacts.

2.2:Objective of EIA

1. To prevent and reduce pollution by avoid, minimize or offset the adverse significant biophysical, social and other relevant effects of development proposals;
- 2.To ensure that environmental considerations are clearly and incorporated into the development decision making process.

3.To protect the productivity and capacity of natural systems and the ecological processes which maintain their functions.

2.3:Background facts

EIA was first introduced in the USA under the Environmental Policy Act (1969). Since then it has evolved and a variety of offshoot assessment techniques have emerged (focusing, for example on social, biodiversity, environmental health and cumulative effects and risk) acting as a broader impact assessment toolkit. In 1990s, many developed and some developing countries designed their EIA legislation. e.g. New Zealand (1991), Canada (1995), Australia (1999), Vietnam (1993), Uganda (1994), Ecuador (1997).

2.4:Brief description of the main steps involved in application of the EIA

Key stages in the Environmental Assessment process include: screening, alternatives, primary assessment, scoping, mitigation, review and monitoring. These need to be managed so that they provide information to decision-makers at every stage of the project .

PHASE I: INITIAL INQUIRIES

- (1) *Understand proposed activity*: Why is the activity being proposed?
- (2) *Screening* (usually by an EIA Authority, or using published checklists) – to decide whether an EIA is required and focus on projects most likely to
 - a. have significant impacts(very high risk). **Do full EIA study**
 - b. those where impacts insignificant (low risk). **EIA process ends**
 - c. Moderate risk . **Do primary assessment**

In general, the outcome of the screening process determines the next step in the EIA process.

(3) Primary assessment - where screening suggests further assessment is needed or if there is uncertainty about the nature of potential impacts (Moderate risk). Uses rapid assessment techniques, but provides sufficient detail to identify key impacts, their magnitude and significance, and evaluate their importance for decision-making. Indicates if a full EIA is needed so start phase two:

PHASE II: FULL EIA STUDY (IF NEEDED)

(1) **Scoping** - a 'narrowing' process usually undertaken by an 'assessment team' to identify the key issues of concern at an early stage in the planning process. It aids site selection and identifies possible alternatives .

(2) **Baseline** - The term "baseline" refers to the collection of background information on the biophysical, social and economic settings proposed project area. Normally, information is obtained from secondary sources , or the gaining of new information through field samplings, interviews, surveys and consultations with the public. The task of collecting baseline data starts right from the period of project inception; however, a majority of this task may be undertaken during scoping and actual EIA. Baseline data is collected for two main purposes:

1. To provide a description of the current status and trends of environmental factors (e.g., air pollutant concentrations) of the host area against which predicted changes can be compared and evaluated in terms of significance.
2. To provide a means of detecting actual change by monitoring once a project has been initiated .

(3) **Identify & choose alternatives** - Consideration of possible alternatives should be undertaken before a choice is made. Some projects can be site specific (e.g. in mining, extraction can only occur where a mineral is sited). In such cases the EIA might focus more on mitigating measures. Projects promoted by public sector agencies are more likely to consider alternative sites .

(4) **Mitigation** - to predict the extent and magnitude of impacts and determine their significance. A variety of methods can be used including: checklists, surveys, matrices, networks, models and simulations, geographical information systems , risk assessment, and economic valuation of environmental impacts. The study should incorporate consideration of mitigating measures - reviewing the action proposed/taken to prevent, avoid or minimize actual or potential significant adverse effects of a project, e.g. modifying a proposal, or substituting techniques using pollution abatement techniques to reduce emissions to legal limits. If the uncertainties are great, with the possibility of critical consequences and no mitigating measures then the project should be rejected.

(5) **Monitoring** – monitoring of project application and operation , and eventually an audit of the project after its completion.