

WATER QUALITY CONTROL

PART III.

Human impact on water resources



3. Human Impact on Water Resources

There are many things that people need to survive, one of which is water. Water is a vital part of life. It is critical that communities, industry, agriculture and the environment receive a continued supply of high quality water. Water is needed by everyone, but while they need it so badly they destroy it. The two major water concerns are quantity, getting enough, and quality, water pollution.

The term "pollution" means the change in the physical, chemical, or biological properties of air, water, or soil that can adversely affect the health, survival, or activities of humans and other living organisms [5]. By pollution of a given element of the environment we can understand the change of the average composition of a given element in "pure" state, as well as occurrence of new components, which concentration is variable in time and space [4].

Classifications of environmental pollutants are very often limited to the following parameters:

- State of aggregation of pollutants;
- Element of the environment to which the pollutants are emitted;
- Type of pollution (chemical, physical, biological or radioactive);
- Emission source of pollutants (land of activity causing emission of a given pollutant).

Changes of the composition of the particular element of the environment caused by emission of certain pollutants are related to the activity of the nature itself and to human activities. As a result of activity of the nature, natural pollutants are emitted. Human activity leads to the emission of pollutants which are called anthropogenic pollutants [4]. Some natural and anthropogenic emission sources are listed in Table 3.1.

All the pollutants (natural and anthropogenic) emitted from a given source are called "primary pollutants". A number of pollutants emitted to the environment can undergo some changes due to reactions with other pollutants, as well as with some components of the environment. Due to these changes primary pollutant concentrations can decrease, but at the same time new compounds often of higher toxicity can be formed [4]. They are called "secondary pollutants".

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Table 3.1. Natural and anthropogenic sources of pollution.

POLLUTION	
Natural sources	Anthropogenic sources
Volcanic eruptions Forest and steppe fires Formation of sea aerosols Emissions of chemicals by plants, animals and human beings Soil erosion Pollen and mold spores Storms (O ₃) Stratospheric intrusion Photochemical reactions	Industry Energy production Use of automotive vehicles Agriculture Waste disposal House keeping

Natural sources of pollution have relatively low significance in causing health and welfare effects, because levels of contaminants are typically very low, and the distances from source and human population is usually large. Moreover, major sources of natural pollution have episodic and transient character.

Anthropogenic sources of pollution are very serious and growing problem, as you can see on the Fig.3.1, due to still increasing human population and its increasing needs.

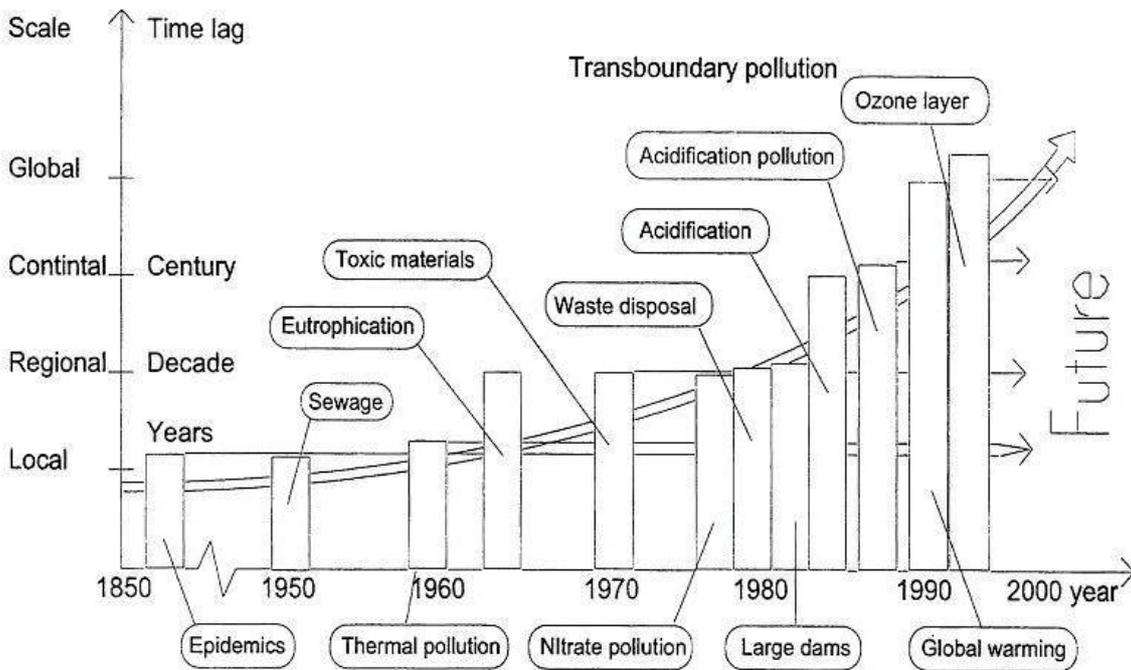


Fig. 3.1. Trends in pollution problems.

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The current interest in the environment stems from the concern that the natural processes are being disrupted by man to such an extent that the quality of life, or even life itself, is being threatened. Many indicators suggest that the world is at a crisis point, for instance the rapid population growth of the world (Fig.3.2) and the consequential growth in energy consumption (Fig 3.3), derived from natural resources. Not only will the earth be depleted of its resources, with the inevitable environmental damage, but there will almost certainly be a parallel increase in waste produced and in pollution of the earth.

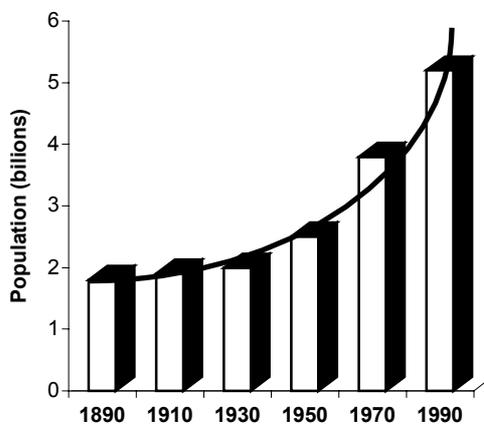


Fig. 3.2. The growth of world population.

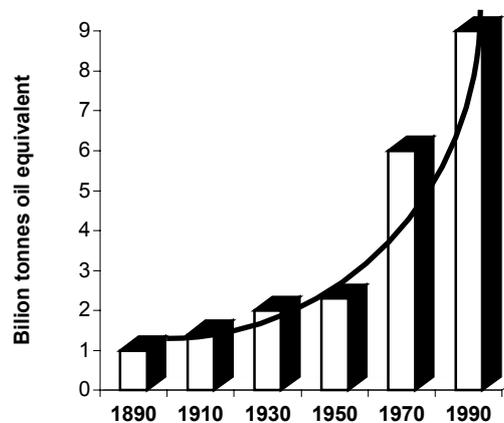


Fig. 3.3. The growth of energy consumption.

Water pollution is any physical, biological and chemical change in water quality that adversely affects living organisms or makes the water unsuitable for desired uses [5]. It occurs when a body of water is adversely affected due to the addition of large amounts of materials to the water. There are many ways that water can be polluted. Although some kinds of water pollution can occur through natural processes, it is mostly a result of human activities.

The sources of water pollution are categorized as being point sources of pollution and non-point sources of pollution:

- Point sources of pollution occur when the polluting substance is emitted directly into the waterway. These are specific locations such as a drain pipe, ditch, or sewer outfall; factories, power plants, sewage treatments, underground coal mines, and oil wells. Point sources are discrete and relatively easy to monitor and treat with discharges that are relatively uniform throughout the year [5].

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- Non-point sources of pollution are scattered or diffuse sources of pollution, having no specific location where they discharge into a body of water. Nonpoint sources include farm fields, lawns and gardens, construction sites, logging areas, roads, streets, and parking lots. These sources are often highly episodic and the concentrations of contaminants are non-uniform. Such sources are difficult to monitor, regulate, and treat.

The major sources of water pollution can be classified as municipal, industrial, and agricultural (Table 3.2).

- Municipal and domestic activities produce large mass of generally non-hazardous wastes. However, all of these, inter alia construction debris, street cleaning, park and landscaping activities, trash dumps, landfills, and sewage, may contaminate ground and surface waters. Institutions like schools and municipal offices are generally treated the same as municipal or domestic activities. However in case of hospitals they should be treated as special wastes because of infectious agents present [5].
- Industrial waste waters can differ considerably both within and among industries. The impact of industrial discharges depends not only on their collective characteristics (BOD, suspended solids) but also on their content of specific inorganic and organic substances;
- Agricultural activities encompass farm operations, food processing (fruit and vegetable, meat and poultry), animal and poultry farms [5]. Agriculture is the source of many organic and inorganic pollutants in surface waters and groundwater. These contaminants include both sediments from erosion of cropland, and compounds of phosphorus and nitrogen that partly originate from animal wastes and commercial fertilizers. Wastes from commercial feeders are contained and disposed of on land. Their main threat to natural waters, therefore, is from runoff and leaching.

Table 3.2. Major sources of water pollution and the use of water.

Main users of water		YEAR							
		Amount of water [km ³] per year							
		1980		1985		1990		1991	
Industry	Uses 2/3 of total	10.1	72%	10.9	70%	9.6	68%	8.9	67%
Municipal	80% comes back as wastes	2.7	19%	2.9	19%	3.0	21%	2.9	22%
Agriculture	2/3 for pond with fish	1.3	9%	1.6	11%	1.7	11%	1.5	11%
Total		14.2	100%	15.5	100%	14.2	100%	13.3	100%

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The chemicals that soaked into the soil gradually work their way into the aquifer, polluting the water and making it unsuitable to use. Once a pollutant gets into the aquifer it is very difficult and expensive to remove it. It is also very hard to detect until damage of water supply will occur.

There are many different effects of water pollution. They include poisoning of drinking water, poisoning of food animals, disruption in balance of rivers' and lakes' ecosystems (which can no longer support full biological diversity), deforestation from acid rains, and many other effects. These effects are, of course, specific to specific contaminant¹.

For dozens of years simultaneously with technology development water pollution become more and more significant.

3.1. The idea of persistence, bioaccumulation, bioconcentration and biomagnification

3.1.1. Persistence and half - life

Persistence defines the "lasting-power" of a compound. The substance is said to be persistent if it physically remains as a discrete chemical entity either in environmental media or in biota for relatively long periods of time (its chemical structure resists environmental physico-chemical degradation and/or metabolic transformation).

Most substances break down or degrade over time as a result of several chemical and microbiological reactions in waters and soils. Sunlight also breaks down some compounds, and such reaction is then called *photodegradation*.

Generally, chemical pathways result only in partial deactivation of compounds, whereas microorganisms can completely breakdown many substances to carbon dioxide, water and other inorganic constituents (biodegradation).

Some compounds produce intermediate substances, called metabolites as they degrade. The biological activity of these substances may also have environmental significance (PAHs, DDT).

¹ See some general information on:
<http://www.epa.gov/owow/nps/qa.html>
<http://www.zephyrus.demon.co.uk/geography/resources/environ/water.html>

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Degradation time is measured in half-time ($t_{1/2}$). Half-time is a measure of the amount of time it takes for one-half of the original amount of a compound in soil and/or water to be deactivated. On the basis of half-time period persistency criteria are described (Table 3.4).

Table 3.3. The criteria of persistency.

Criteria of persistency	Half-time $t_{1/2}$
Air	> 30 days
Soil, sediment, water, sludge	> 50 days

Half-time is sometimes defined as the time required for half the amount of substance to be completely degraded and released as carbon dioxide. Usually, the half-time of a substance measured by the latter basis is longer than that based on deactivation only. This is especially true if toxic or non-toxic metabolites accumulate in the soil during the degradation.

3.1.2. Bioconcentration

Bioconcentration is the intake of chemical contaminants through an organism's epithelial tissues or gills, and the subsequent concentration of that chemical contaminant within the organism's tissues to a level that exceeds ambient environmental concentrations.

Although the process is the same for both natural and manmade chemicals, the term bioconcentration usually refers to chemicals foreign to the organism [14].

The degree to which a contaminant will concentrate in an organism is expressed as a bioconcentration factor (BCF), which is defined as the concentration of a chemical in an organism's tissues divided by the exposure concentration [51].

$$\text{Bioconcentration factor} = \frac{\text{Concentration of a compound in an organism}}{\text{Concentration of a compound in surrounding water}}$$

Thus, a BCF of 100 means that the organism concentrates that chemical to a concentration 100 times greater than in the surrounding media. Bioconcentration factors are most commonly applied to aquatic organisms such as fish or aquatic invertebrates. Within a species, bioconcentration factors differ for different chemical compounds. BCFs also vary among species for the same contaminant and site-specific environmental conditions can affect BCFs [51].

3.1.3. Bioaccumulation

Bioaccumulation is the process by which chemical contamination in organisms increases with each step in the food chain [15].

Bioaccumulation affects animals that are higher in the food chain through contaminant build-up over time. Older animals contain a higher concentration of contaminants because they have been consuming and storing contaminants longer. So the younger the animal harvested, generally the lower the amount of contaminants they will have [43].

Bioaccumulation is a normal process that can result in injury to an organism only when the equilibrium between exposure and bioaccumulation is overwhelmed, relative to the harmfulness of the chemical [44].

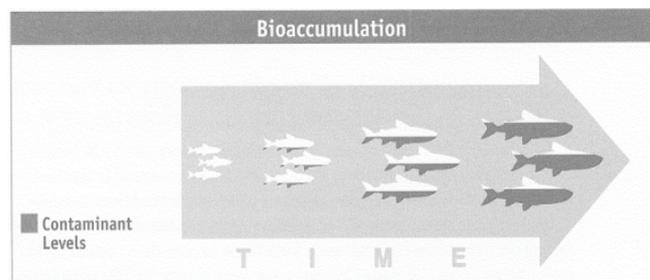


Fig.3.4. The bioaccumulation scheme [49].

Uptake and storage of the chemical is affected by its solubility in water and fats. The time between uptake and eventual elimination of a chemical directly affects bioaccumulation. Chemicals that are immediately eliminated do not bioaccumulate [44].

The extent of bioaccumulation depends on:

- Concentration of a chemical in the environment;
- Amount of chemical coming into an organism from the diet, water, or air;
- Time necessary for the organism to acquire the chemical and then excrete, store, and/or degrade it;
- Duration of exposure.

Understanding sources, pathways and bioaccumulation is critical to developing effective remediation plans for contaminated ecosystems. The most effective plan is the one that remediates the contaminants at their source [45].

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Example:

A typical food chain includes algae (or organic matter from the surface of sediment bed) eaten by the water flea eaten by a small fish eaten by a predatory fish and finally consumed by an osprey (or human being). If each step results in increased bioaccumulation, then an animal at the top of the food chain, through its regular diet, may accumulate a much greater concentration of chemical than was present in organisms lower in the food chain.



Fig.3.4. An aquatic food chain, from plankton and benthic invertebrates through forage and predatory fish, to avian predators [45].

3.1.4. Biomagnification

Biomagnification is the process by which chemical contaminants are concentrated at levels that exceed chemical equilibrium from dietary absorption of the chemical [15].

Biomagnification occurs when some chemicals become increasingly concentrated at successively higher trophic levels of a food chain (the dietary linkages between single-celled plants and increasingly larger animal species). Longer food chains result in greater biomagnification at each higher level [43].

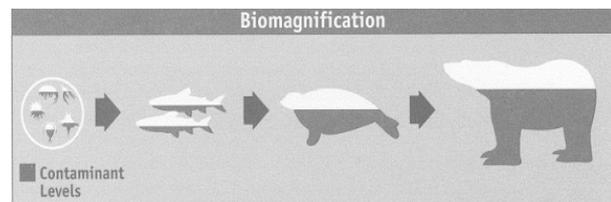


Fig.3.5. The biomagnification scheme [49]

Through biomagnification, the concentration of a chemical in the animal at the top of the food chain may be high enough to cause death or adverse effects on behaviour, reproduction, or disease resistance and thus endanger that species, even when levels in the water, air, or soil are low. Fortunately, bioaccumulation does not always result in biomagnification [44].

The bioconcentration, bioaccumulation, and biomagnification of chemical contaminants in marine biota are dynamic processes that involve many interconnected variables. For example, the potential of a chemical to bioconcentrate, bioaccumulate, or biomagnify in organisms and

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food webs is dependent upon the properties of the chemical (e.g. hydrophobicity, lipophilicity, and resistance to degradation), environmental factors (e.g. salinity, temperature, concentration of other organic chemicals, and redox potential), biotic factors (e.g. the organism's mode of feeding, trophic position, lipid concentration, and metabolism), and bioavailability (e.g. current chemical inputs, transport mechanisms, and degree of contamination) [16, 17].

3.2. Eutrophication

Urban and industrial emissions of wastewater were one of the first environmental problems. They were already causing problems at the beginning of the 20th century, in the form of stench, filth and infections. Their abundant content of organic material was gradually broken down by micro-organisms in water, but this kind of degradation consumes oxygen, producing knock-on effects in the form of oxygen deficiency and fish kill. In addition, wastewater contained large quantities of nutrients. This nutrient increment caused heavy eutrophication of the waters receiving the emissions.

Eutrophication (*Greek- eutrophos - 'well nourished'*) refers to an increase in the rate of supply of organic matter to an ecosystem, which most commonly is related to nutrient enrichment enhancing the primary production in the system. Nutrients are vital for aquatic life. But the presence of excessive nutrients can seriously disturb the functioning of ecosystems [42].

It is necessary to distinguish between two kinds of eutrophication:

- Natural eutrophication, and
- Cultural (anthropogenic) eutrophication.

Eutrophication is a natural process which has been going on ever since the lakes were formed after the glacial period. It was initially limited to lakes, where little water movement and limited matter exchange favoured rapid biomass growth [4]. Today the process takes place also in flowing waters - mainly in storage reservoirs, and to a much lesser extent in rivers. The rate of the process is different in various basins. The eutrophication process has been rapidly accelerated in modern times due to human activities; hence it has now anthropogenic character [4].

Eutrophication occurs to all lakes over time as the weathering of rocks and soils from the surrounding catchment area leads to an accumulation of nutrients in water and associated

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sediments. Input of plant nutrients (Table 3.3) from watershed runoff or sewage is also extremely important² [28].

Natural eutrophication is the process by which lakes gradually age and become more productive. It normally takes thousands of years to progress and include the following stages: oligotrophy, mesotrophy, and eutrophy (Table 3.4) [9].

Table 3.3. Essential Plant Nutrients: Sources and Functions [3].

Nutrient	Source	Function
Macronutrients		
Carbon (CO ₂)	Atmosphere, decay	Biomass constituent
Hydrogen	Water	Biomass constituent
Oxygen	Water	Biomass constituent
Nitrogen (NO ₃ ⁻)	Decay, atmosphere (from nitrogen-fixing organisms), pollutants	Protein constituent
Phosphorous (phosphate)	Decay, minerals, pollutants	DNA/RNA constituent
Potassium	Minerals, pollutants	Metabolic function
Sulphur (sulphate)	Minerals	Proteins, enzymes
Magnesium	Minerals	Metabolic function
Calcium	Minerals	Metabolic function
Micronutrients		
B, Cl, Co, Cu, Fe, Mo, Mn, Na, Si, V, Zn	Minerals, pollutants	Metabolic function and/or constituent of enzymes

Oligotrophy is the beginning stage of a lake. Young lake (and man made reservoirs) usually is rich in dissolved oxygen, but have low levels of nutrients and correspondingly low levels of biological activity [52]. This means that the lake also has a lack of fertility that limits animal life in the lake. In its mid-life, the lake becomes mesotrophic. The nutrients flowing into the lake accumulate in the bottom sediments along with nutrients that settle from decay of the lake's own organisms. Some of this nourishment recycles into the upper waters where it is photosynthesized into greater production of phytoplankton [53].

The final stage of lake's ageing is eutrophy. This stage occurs when the lake becomes old. Old lakes usually have high levels of nutrients and correspondingly high levels of biological activity [52]. The lake's water becomes turbid with decaying organic matter from plants and animals and the supply of dissolved oxygen in the water becomes depleted by the rapidly

² See examples of eutrophication on <http://drake.marin.k12.ca.us/stuwork/rockwater/Eutrophication/examplespage.html>

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growing plants. The absence of oxygen causes anaerobic bacteria to attack organic matter thus releasing hydrogen sulphide. This signifies the lake's turning into a swamp or bog [53].

Table 3.4. Different levels of lake eutrophication.

Trophic States	Lake Characteristics
Oligotrophic	Clear waters with little organic matter or sediment and minimum biological activity.
Mesotrophic	Waters with more nutrients, and therefore, more biological productivity.
Eutrophic	Waters extremely rich in nutrients, with high biological productivity. Some species may be choked out.

The natural time scale for the aging of a lake from being oligotrophic to eutrophic is of the order of thousands of years. To renew all the water in a lake may take up to a hundred years compared to a few days for the renewal of the water in a river. Consequently, lakes are particularly susceptible to pollution such as artificial eutrophication [52].

The nutrient status of any environmental water is determined by the supply of nutrients from its catchment, which in turn is influenced by the geology. Thus waters will vary in their natural nutrient status. Some waters are naturally eutrophic. However enrichment and consequential impacts can occur if there are changes to the nature of the catchment [54].

Although eutrophication is a natural process human activities can greatly accelerate eutrophication by increasing the rate at which nutrients and organic substances enter aquatic ecosystems from their surrounding watersheds. Agricultural runoff, urban runoff, industrial wastes, leaking septic systems, sewage discharges, eroded stream banks, and similar sources can increase the flow of nutrients and organic substances into aquatic systems [28].

To understand why human activity can greatly accelerate the eutrophication process, it is necessary to refer to Table 3.3, which shows the chemical elements needed for plant growth. Most of these are present at a level more than sufficient to support plant life in the average lake or reservoir. Hydrogen and oxygen come from the water itself. Carbon is provided by CO₂ from the atmosphere or from decaying vegetation. Sulphate, magnesium, and calcium are normally present in abundance from mineral strata in contact with the water. The micro-nutrients are required at only very low levels. Therefore, the nutrients most likely to be limiting are the "fertilizer" elements: **nitrogen** in the form of nitrate, nitrite or ammonium, **phosphorus** in the form of ortho-phosphate, and **potassium** [3].

Each of these elements can come from natural sources - phosphorus and potassium from mineral formations, and nitrogen fixed by bacteria, blue-green algae, or discharge of lightning

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in the atmosphere [3]. Fertilizer elements (nitrogen, phosphorus, potassium) are all present in sewage and are found in runoff from heavily fertilized fields. They are also constituents of various kinds of industrial wastes (Table 3.5).

Table 3.5. The contributions (in percentage terms) of the main sources of phosphorus entering surface waters in the UK; The source of these figures is Morse et al, The economic & environmental impact of phosphorus removal from wastewater in the European Community, Selper Publications, London 1993.

Agricultural	43%
Human and household waste including detergents	43%
Industry	8%
Background source	6%

Run-offs from arable areas can contain large amounts of nitrogen and phosphorus compounds used as fertilizers. The amount of nutrients carried by run-offs depends on the agricultural knowledge, i.e. on the kind of crops, terms and manners of fertilizer application, etc. Nitrogen compounds which are water-soluble readily reach surface waters. Phosphorus compounds are less soluble and are adsorbed on soil particles. They reach surface waters mainly as a result of erosion [4].

Apart from run-offs, also precipitation can be an important source of nitrogen and phosphorus. It can contain ammonium nitrogen, nitrate nitrogen, phosphorus and potassium. Such precipitation can directly pollute water basins. It can also fall on the soil surface and reach water basins together with run-offs [4].

Since phosphorus and nitrogen are natural fertilizers their addition results in the mass production of algae and other plant life in the lakes and ponds [9]. When plants and algae die their remains gradually sink and are consumed by aerobic bacteria. This results in a reduction of the level of dissolved oxygen. Eventually, often near the bottom of a lake, virtually no oxygen remains and the water is said to be anoxic. The worst affected areas can become completely anoxic [42]. Under these conditions anaerobic bacteria flourish. Anaerobic bacteria often produce foul-smelling compounds such as hydrogen sulphide (H_2S), thioalcolohs (RSH) and ammonia (NH_3), resulting in the water becoming extremely unpleasant [52]. Moreover, release of toxic hydrogen sulphide can poison organisms and make the reservoir lifeless. When there is no oxygen left for the organisms they soon die and sink to the bottom of the lake. This only acts as more fertilizer for the lake and the lake is eventually taken over by the plant life [42].

3.2.1. Effects of Eutrophication

Elevated levels of nutrients can change a water body's natural balance. Eutrophication can have both temporary and more irreversible effects on aquatic ecosystems. The effects of the changes which occur depend on the water body. Excessive nutrient inputs into a water body induce biological, chemical and physical changes in aquatic plant and animal communities. [54].

Among the main **biological effects** of eutrophication are:

a. Algal bloom

An algal bloom is a rapid and excessive growth of algae [58]. It can affect the water quality in several ways.

Motile algae species will crowd the water surface to capture light, creating super-saturated oxygen conditions and raising the pH as they photosynthesise (increased chlorophyll concentration). When the bloom starts to die off, the organic matter accumulates at the bottom of the water body. The bacteria breaking down this matter use up considerable amounts of oxygen, and in some cases growth and/or decay of benthic (bottom-dwelling) mats can create anoxic conditions close to the sediments [57].

Certain algal species can produce toxins, which may seriously affect the health of mammals (including humans), fish and birds. This occurs either through the food chain, or through contact with, or ingestion of, the algae. Eutrophication ultimately detracts from biodiversity, through dominance of nutrient-tolerant plants and algal species. These tend to displace more sensitive species of higher conservation value, changing the structure of ecological communities [54].

b. Change in species composition

Eutrophic water bodies are highly productive; however the nutrient rich conditions will only favour some plant and animal species. This means that as productivity or biomass increases, often biodiversity will decrease. Opportunistic species will take advantage of the favourable conditions, rapidly reproducing with the onset of increased nutrient concentrations. Algae are particularly responsive to nutrient pulses, and under certain conditions the population can be

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dominated by potentially harmful species. For the animals using the algae as a food source, their numbers will also grow [57].

- c. Disappearance of commercially important species (such as trout) [52].

Physical effects consist in deterioration of physical properties of water. These are:

- a. Change in water colour and ability of light penetration

Greenish, murky water is typically the first sign of eutrophication as microscopic plants and algae grow profusely, consuming the surplus nutrients. Being produced faster than consumed, algae forms mats due to which penetration of light into the water is diminished. Diminished light penetration decreases the productivity of plants living in the deeper waters (and hence their production of oxygen) [57].

- b. Increased vegetation may impede water flow and the movement of boats;
- c. Decrease in the amenity value of the water (e.g. It may become unsuitable for water sports such as sailing);
- d. Reduced recreational value and income from tourism [52].

Chemical effects of eutrophication are the following:

- a. Oxygen depletion

A side effect of algal blooms is oxygen depletion. Water in the environment generally contains a small amount of dissolved oxygen. When organic material decomposes, oxygen is consumed. After an algal bloom large quantities of algae decompose, using much of the available oxygen in water [58]. Oxygen concentration in water is also lowered by the lack of primary production in the darkened, deeper waters [59].

The lack of oxygen not only can kill water life and disrupt the ecology of a water body but also accelerate the release of nutrients and pollutants from the sediments. Nutrients and toxic heavy metals bonded to the sediments are quite harmless. When the water becomes anoxic the nutrients and heavy metals are released due to a chemical changes. The nutrients released can lead to further algal blooms and eutrophication development. The heavy metals released can enter the food chain [58].

- b. The water may become unsuitable for drinking, even after treatment [52].

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3.2.2. Managing Aquatic Eutrophication

Although eutrophication is only a problem because of human interaction, its effects can be just as harmful to humans as they are to the environment. There are an unlimited number of reasons why the unnatural acceleration of eutrophication is dangerous to humans.

One of the most important is methylation of mercury and its bioaccumulation. In many lakes and rivers mercury from the chemical waste dumped in the water collects on the algae inside. The bacteria in the water transform the mercury into methyl mercury, which is an incredibly harmful, if not lethal, substance and bioaccumulate along the food chain. As long as mercury and other extremely harmful chemicals are put into our lakes and ponds, there is always a chance that they will creep into our food and drinking water [7].

Aquatic eutrophication, where environmental waters are enriched by nutrients deriving from human activities, can cause adverse effects on both the ecology and the uses of waters. Whilst the control of eutrophication is recognised as a long term commitment regular reports on the extent of eutrophication and progress of the management strategies are needed³.

Example:

Scientists from Canada used small, natural lakes as experimental systems to determine which of the major plant nutrients (carbon, nitrogen, phosphorus) was the key to controlling cultural eutrophication in lakes. Over a number of years, different lakes were experimentally fertilized in various ways. One of the lakes (Fig.3.6) was divided into two approximately equal portions using a plastic divider curtain. Carbon and nitrogen were added to one half of the lake, while carbon, nitrogen and phosphorus were added to the other half. For eight consecutive years, the side receiving phosphorus developed eutrophic algal blooms, while the side receiving only carbon and nitrogen did not (see photo, below). The sections on the upper part of the picture had carbon and nitrogen put into it and the other section had carbon, nitrogen and phosphate put in to see which element was the most harmful cause of sped up eutrophication. As one can see, the part with phosphate changed and became high in nutrients where the other one basically stayed the same [19].

³ Eutrophication in Europe's coastal waters – reports:
http://reports.eea.eu.int/topic_report_2001_7/en/Topic_Report_7_2001.pdf
http://reports.eea.eu.int/topic_report_2001_7/en/topic7_part1.pdf
http://reports.eea.eu.int/topic_report_2001_7/en/topic7_part2.pdf
http://reports.eea.eu.int/topic_report_2001_7/en/topic_report_7_summary.pdf

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Fig.3.6. Experimental lake. The bright green colour results from bluegreen algae (Cyanobacteria), which are growing on phosphorus added to the near side of the curtain.



Fig. 3.7. Experimental lake. The bright green colour caused by algae stimulated by the experimental addition of phosphorus for the 26th consecutive year. Lake in the background is unfertilized.

3.3. Acidification and Acid Rain

Acidification is defined as a decline in nature's ability to neutralise acid precipitation, which in turn lowers the pH of soil and water bodies. The main causes of acidification are airborne compounds of sulphur (mainly SO_2) and nitrogen [68].

Sulphur dioxide (SO_2) is chiefly formed in the combustion of oil and coal. These fossil fuels come from the plant material, hundreds of millions of years ago metamorphosed into oil, coal and natural gas. Everything organic takes up sulphur which explains its presence in fossil fuels. The concentrations vary, however. Crude oil usually contains anywhere from one-tenth to between two and three percent of sulphur by weight. In coal the levels vary even more, whereas natural gas contains considerably lesser sulphur quantities [4].

The other remarkable cause of acidification is emissions of nitrogen oxides. These consist mainly of nitrogen monoxide (NO) and nitrogen dioxide (NO_2) which are usually grouped under the collective term NO_x . Nitrogen oxides are formed in all types of combustion. Unlike sulphur dioxide, which comes entirely from the sulphur contained in the fuel or raw material, most of nitrogen oxides are formed by the reaction of nitrogen gas in the combustion air with oxygen. The higher the combustion temperature, the more nitrogen oxide will be formed. Also contributing to the process is the nitrogen in the fuel itself. The largest single source of nitrogen oxide is road traffic. Certain types of fertilizers are another source of nitrogen

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pollution. Crop lands treated with liquid commercial fertilizers and animal manure emit large quantities of ammonia to the atmosphere. Ammonia actually causes a rise in pH of precipitation, but the effect is eliminated when ammonium ions (NH_4^+) in the rain or snow are converted by microorganisms in the soil or absorbed for instance by trees after descending to the ground [4].

Susceptibility to acidification is affected by the level of acid precipitation, and by the natural buffering capacity of the waterway or soil in question [68].

Acid rain is precipitation that has been polluted by emissions of sulphur dioxide (SO_2) and/or oxides of nitrogen (mainly NO_2 and NO_3 called NO_x) in the atmosphere. SO_2 and NO_x can be naturally found in the atmosphere. Industrialisation has however, led to a dramatic increase of concentration of these substances. The sources of these oxides are basically burning of fossil fuel: coal, oil and gas, but also road traffic, ships and metallurgic or ferro-alloy industry.

Pure water has a pH of 7.0. Normal or unpolluted precipitation is slightly acidic, having a pH ranging from 5.6 to 5.0. The slight acidity of normal precipitation is due to atmospheric carbon dioxide and other acidic materials including sulphate of natural origin which are absorbed during the precipitation process.



Acid rain has acidity values that are up to ten times greater than normal precipitation primarily due to the incorporation of airborne pollutants of man-made origin.

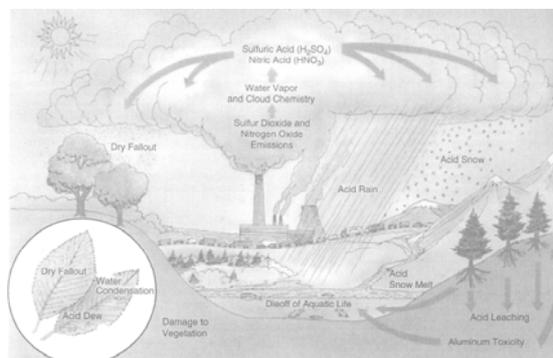


Fig.3.8. Acid precipitation [5].

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Nitrogen and sulphur oxides react with water vapour, form sulphuric acid and nitric acid and then fall to the earth as wet deposition. Wet deposition refers to acidic rain, fog, and snow (Fig. 3.8). As this acidic water flows over and through the ground, it affects a variety of plants and animals. The strength of the effects depend on many factors, including how acidic the water is, the chemistry and buffering capacity of the soils involved, and the types of fish, trees, and other living things that rely on the water.

Nitrogen and sulphur compounds can also fall to the earth in dry form such as gases and dust. About half of the acidity in the atmosphere falls back to earth through dry deposition. The deposition of dry materials is dependent on the chemical species and differs with surface characteristic and meteorological conditions. Prevailing winds transport the compounds, sometimes hundreds of miles, across state and national borders. The wind blows these acidic particles and gases onto buildings, cars, homes, and trees. Dry deposited gases and particles are sometimes washed from trees and other surfaces by rainstorms. When that happens, the runoff water adds those acids to the acid rain, making the combination more acidic than the falling rain alone. The combination of acid rain plus dry deposited acid is called *acid deposition* [69].

Example:

Oxides of sulphur and nitrogen can be carried long distances - thousands of kilometres - by the air. This means that the problem of acidification recognizes no borders.

Precipitation over eastern North America and over much of Europe has acidity values that are up to ten times greater than normal primarily due to the incorporation of airborne pollutants of man-made origin. As an example, the average pH of precipitation in central Ontario is about 4.2. Measurements have revealed that the acidity of cloud water droplets atop Whiteface Mountain in New York was as high as pH 2.6. This cloud moisture is about one thousand times as acidic as normal rain. In some areas, the pH of precipitation may exceed 5.6, as in the Canadian Prairie Provinces where wind-blown alkaline soil materials actually reduce the natural acidity levels [19].

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European maps of critical loads of acidity (Fig.3.9), sulphur and nitrogen have been produced to assess the sensitivity of forest soil and surface waters. These maps can be compared with present and projected levels of pollutant emissions, allowing assessment of the effects of various emissions abatement strategies. Parts of central and northwest Europe currently receive 20 times or more acidity than their critical loads, thus affecting the long-term sustainability of these ecosystems [4].

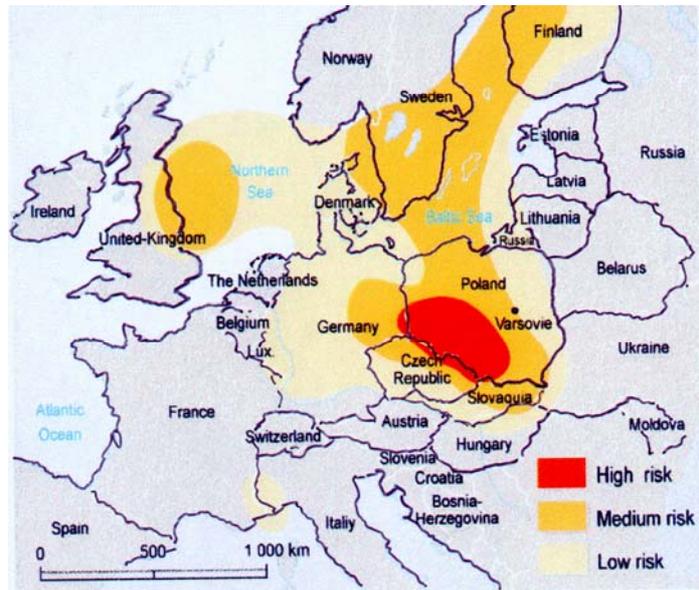


Fig.3.9. Critical loads of acidity in Europe. Parts of central and northwest Europe currently receive 20 times or more acidity than their critical loads, thus affecting the long-term sustainability of these ecosystems.

3.3.1. Formation of Acid Rain

In spite of the apparent simplicity, the process of acid rain formation from primary pollutants such as SO_2 and NO_2 is very complex [4]. Sulphur dioxide excited by solar radiation (sunlight) is oxidized by atmospheric oxygen to SO_3 which on reaction with water vapour gives sulphuric acid, converted in turn to sulphates by the reaction with various chemical elements present in atmospheric aerosols. H_2SO_4 formation from atmospheric SO_2 can be described by the following reaction [18]:

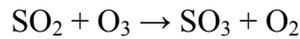


The rate of photochemical SO_2 oxidation by atmospheric oxygen in pure atmosphere (with no pollutants) is quite small and ranges from 0.1 to 0.5 %/h. The reaction is very important since it initiates the chain of other reactions. Therefore, over relatively clean regions, SO_2 is the main sulphur pollutant [4]. Oxidation proceeds especially easily in the air highly contaminated with industrial dusts containing oxides of iron, manganese, magnesium and calcium. These oxides are strong catalysts of oxidation of SO_2 to SO_3 . Sulphur trioxide

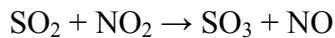
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formed dissolves easily in water droplets. Thus the final product of SO₂ oxidation in the atmosphere is H₂SO₄ aerosol [4].

Nitrogen oxides in the atmosphere generate large amounts of ozone, necessary for oxidation of SO₂ according to the reaction [18]:

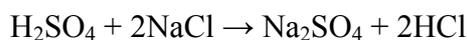


Direct reaction of nitrogen dioxide with SO₂ also occurs, although very slowly:



On the other hand, hydrocarbons react with SO₂ generating aerosols of unpleasant smell and considerable toxicity. These aerosols form fog of a complex composition, being a mixture of highly oxidized, strong organic acids containing sulphur, like sulphanilic acid, disulphuric acid or disulphonic acid.

Apart from the H₂SO₄ mist, the final products of SO₂ reactions in the atmosphere comprise also sulphates, formed in reactions of SO₃ and with various elements contained in atmospheric aerosol. The presence of gaseous ammonia in the atmosphere causes intensive neutralization of SO₂, which rapidly disappears. The reaction of SO₂ with NH₃ yields ammonium sulphate aerosol. Also sea aerosol reacts with H₂SO₄ forming ammonium sulphate, yet this reaction yields also highly toxic hydrogen chloride aerosol [4]:



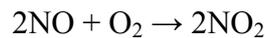
As a result of the above discussed transformations of SO₂ in urban-industrial regions the rate of SO₂ removal is 2 - 20% per hour. Half-life of SO₂ in industrialized regions is estimated to be 4 - 6 h, while in agricultural - forest regions it can be more than ten hours [4].

Nitrogen oxides (NO_x) are another class of pollutants prone to rapid physicochemical changes in the atmosphere. Three nitrogen oxides occur in the atmosphere:

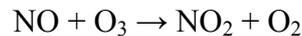
- nitrous oxide N₂O,
- nitric oxide NO,
- nitrogen dioxide NO₂.

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Nitrous oxide is emitted to the atmosphere as a result of natural biological processes in soil fertilized with nitrogen fertilizers. Hence, this compound is found at certain concentrations in agricultural regions. Air of urban-industrial agglomerations contains mainly nitric oxide and nitrogen dioxide. Combustion of fossil fuels produces mainly nitric oxide. Following the temperature drop along the stack this compound is partly oxidized according to the reaction [4]:



After leaving the stack NO reacts mainly with ozone, forming NO₂:



Apart from the above discussed reactions of oxygen and ozone with nitrogen oxides, also other reactions take place (e.g. with water):



As a result of all these reactions certain equilibrium is reached in the atmosphere between O₃, NO and NO₂ [4].

3.3.2. Environmental Effects of Acid Rain

An acidic dry deposition together with acidic rain can cause degradation of the environment in many different ways. They can affect not only aquatic ecosystems but also terrestrial ecosystems, manmade structures and many different aspects of human life.

a. Acidification of surface waters

The ecological effects of acid rain are most clearly seen in the aquatic environments, such as streams, lakes, and marshes. Acid rain flows directly into streams, lakes, and marshes or with run-off after falling on forests, fields, buildings, and roads. Most lakes and streams have a pH between 6 and 8, although some lakes are naturally acidic even without the effects of acid rain. Acid rain primarily affects sensitive bodies of water, which are located in watersheds

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whose soils have a limited buffering capacity. Lakes and streams become acidic when the water itself and surrounding soil cannot buffer the acid rain enough to neutralize it.

The consequence of water changes in pH values is a gradual dying out of microorganisms and larger organisms which are sensitive to changes in acidity, for example snails, mussels, leeches, crustaceans, mayfly larvae and fish [69]. In strongly acidified lakes fish perish, and after some time life in the water reservoir becomes dominated by only few plant and animal species [4].

High concentration of hydrogen ions in acidified waters is not the only reason for plants and animals becoming ill and dying [4]. As acid rain flows through soils in a watershed, aluminium is released from soils into the lakes and streams located in that watershed. So, as pH in a lake or stream decreases, aluminium levels increase. Both low pH and increased aluminium levels are directly toxic to fish. In addition, low pH and increased aluminium levels cause chronic stress that may not cause death of fish, but leads to lower body weight and smaller size and makes fish less able to compete for food and habitat.

In acidic waters concentration of such metals as cadmium, zinc and lead also increases. These metals when present in soluble forms are taken up by plants and animals much more easily [4].

	pH 6.5	pH 6.0	pH 5.5	pH 5.0	pH 4.5	pH 4.0
TROUT	Shaded	Shaded	Shaded	Shaded	Black	Black
BASS	Shaded	Shaded	Shaded	Black	Black	Black
PERCH	Shaded	Shaded	Shaded	Black	Black	Black
FROGS	Shaded	Shaded	Shaded	Shaded	Shaded	Shaded
SALAMANDERS	Shaded	Shaded	Shaded	Shaded	Black	Black
CLAMS	Shaded	Shaded	Black	Black	Black	Black
CRAYFISH	Shaded	Shaded	Shaded	Black	Black	Black
SNAILS	Shaded	Shaded	Black	Black	Black	Black
MAYFLY	Shaded	Shaded	Shaded	Black	Black	Black

Fig. 3.10. pH tolerance. Different species.

Some types of plants and animals are able to tolerate acidic waters. Others, however, are acid-sensitive and will be lost as the pH declines. Generally, the young of most species are more sensitive to environmental conditions than adults. At pH 5, most fish eggs cannot hatch. At lower pH levels, some adult fish die. Some acid lakes have no fish. Fig. 3.10 shows that not all fish, shellfish, or the insects that they eat can tolerate the same amount of acid; for example, frogs can tolerate water that is more acidic (has lower pH) than trout [29].

The impact of nitrogen on surface waters is also critical. Nitrogen plays a significant role in episodic acidification and new research recognizes the importance of nitrogen in long-term chronic acidification as well. Furthermore, the adverse impact of atmospheric nitrogen deposition on estuaries and near-coastal water bodies is significant. Scientists estimate that from 10 - 45 % of the nitrogen produced by various human activities that reaches estuaries

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and coastal ecosystems is transported and deposited via the atmosphere. Nitrogen is an important factor in causing eutrophication of water bodies [29].

b. Liberation of heavy metals deposits in soil

Due to the action of acid rains on heavy metal dusts entering soil as a result of deposition from the atmosphere, soluble compounds of these metals are formed. Many toxic metals are held in the ground in compounds. However, acid rain can break down some of these compounds, freeing the metals and washing them into water sources such as rivers. These metals are then more easily assimilated by cultivated plants, with which they can enter human organisms [4].

As the water becomes more acidic, it can also react with lead and copper water pipes, contaminating drinking water supplies.

c. Degradation of forests and trees

Acid rain has been implicated in contributing to forest degradation, especially in high-elevation spruce. Pollution can affect trees directly and indirectly. In the first case we observe the damage of needles and leaves. This is due to the damage (caused, e.g., by SO₂ dry deposition, ozone or acid rain) of the protective layer of wax covering needles or damage of the stomatal apparatus which controls transpiration rate. Inside leaves and needles various membranes can be damaged, which can adversely affect the nourishment system and water balance.

Indirect damages result from soil acidification. A spring shower in the forest washes leaves and falls through the trees to the forest floor below. Some trickles over the ground and runs into a stream, river, or lake, and some of the water soaks into the soil. That soil may neutralize some or all of the acidity of the acid rainwater. The ability of forest soils to resist acidity depends on the thickness and composition of the soil, as well as the type of bedrock beneath the forest floor [29].

Acid rain soaks through forest floor, reaches mineral subsoil and liberates aluminium ions from below the humus layer. Lowered pH together with toxic action of some metals lead to root damage, especially capillary vessels. As a result, roots are unable to take up sufficient amounts of nutrients and water. A tree weakened in such a way is then easily attacked by pests and fungi. A pathological wet core is formed in the trunk, which stops transport of water to higher parts of the tree. The dramatic disturbance of water balance can explain why

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coniferous trees (dying of for trees constitutes a similar problem as that of spruces) die first from the top and from inside [4].

There is good reason to believe that long-term changes in the chemistry of some sensitive soils may have already occurred as a result of acid rain. As acid rain moves through the soils, it can also strip away vital plant nutrients through chemical reactions, thus posing a potential threat to future forest productivity [69].

Deciduous trees are not so sensitive because the total surface area of leaves, i.e., the surface exposed to pollutants is smaller, and because the leaves fall every year and thus are exposed to pollutants for a shorter period of time [4].

The change in the Mg/Al and Ca/Al ratio in the soil solution during the soil acidification affects root growth. The primary effect appears to be a substitution of Ca and Mg by Al in the secondary cell wall, which affects its extension growth. In addition to interaction with Al root growth is also affected by a changing $\text{NH}_4/\text{cation}$ ratio. An increase of ammonium in the soil solution of the humus layer has been observed in acidifying soils which is probably a result of the recent increase of deposition of ammonium from the atmosphere, as well as from a reduced microbial activity in acid soils. The Mg/Al and Mg/ NH_4 ratios affect not only root growth but also the uptake of cations. Ca and Mg are reduced in the presence of Al and NH_4 . In addition, nitrate uptake is inhibited in the presence of NH_4 [4].

d. Plants damage

Acid rain can harm other plants in the same way it harms trees. Although damaged by other air pollutants such as ground level ozone, food crops are not usually seriously affected because farmers frequently add fertilizers to the soil to replace nutrients that have washed away. They may also add crushed limestone to the soil. Limestone is an alkaline material and increases the ability of the soil to act as a buffer against acidity. This worsens crops and makes additional liming necessary [29]. Crop decrease is observed when SO_2 concentration exceeds $80 \mu\text{g}/\text{m}^3$ (annual mean value). In Poland sour soils constitute 83% (highly and medium sour soils - 58%) of all the arable land. Excessive concentration of hydrogen ions decreases soil sorption capacity with respect to nutrients (and fertilizers) [4].

e. Soil acidification

Sensitivity to acidification is greatest in areas where the minerals in the soil weather slowly. When the soil becomes acidified its essential nutrients are leached out, which reduces the

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fertility of the soil. The acidification process also releases metals that can harm the micro-organisms in the soil that are responsible for decomposition, as well as birds and mammals higher up the food chain, including man [69].

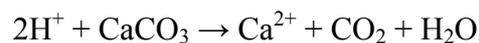
f. Visibility reduction

Sulphates and nitrates that form in the atmosphere from sulphur dioxide emissions contribute to visibility impairment [29].

Sulphur dioxide emissions lead to the formation of sulphate particles in the atmosphere. The final product of SO₂ oxidation in the atmosphere is H₂SO₄ aerosol with particle diameter depending on relative air humidity, from 0.4 to 0.8 μm. Since particles of such size strongly disperse sunlight, a considerable decrease in daytime visibility is the first effect of H₂SO₄ aerosol occurrence [69].

g. Materials deterioration

Acid rain and the dry deposition of acidic particles contribute to the corrosion of metals (such as bronze) and deterioration of stone (such as marble and limestone) and paint on buildings, cultural objects, and cars. Because of the effect of hydrogen ion worst affected are objects and structures of easily weathered materials, such as limestone CaCO₃ [3]:



In acidified soil and water indirect corrosion which damages concrete foundations and steel structures takes place [4]. These effects seriously reduce the value of buildings, bridges, cultural objects (such as statues, monuments, and tombstones), and cars.

Dry deposition of acidic compounds can also dirty buildings and other structures, leading to increased maintenance costs. To reduce damage to automotive paint caused by acid rain and acidic dry deposition, some manufacturers use acid-resistant paints [29].

h. Human health

Based on health concerns, SO₂ has historically been regulated under the Clean Air Act. Sulphur dioxide interacts in the atmosphere to form sulphate aerosols, which may be transported long distances [69] by winds and inhaled deep into people's lungs. Fine particles can also penetrate indoors. Many scientific studies have identified a relationship between

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elevated levels of fine particles and increased illness and premature death from heart and lung disorders, such as asthma, emphysema, fibrosis and bronchitis.

3.3.3. What Should Be Done?

Because intensity of sulphur emissions have started to fall one may think that the danger of acidification is over. However, acidification continues to get worse in many areas - albeit at a slower rate than before. The problem will only be solved when emissions of acidifying pollutants fall below a level that nature can tolerate and neutralize.

To achieve this, major reductions in emissions are still required. Reduction in SO₂ emissions should significantly decrease or slow down the acidification of water bodies, many acidified lakes and streams will improve substantially so that they can once again support fish life, and will reduce stress to forests. In addition, visibility will be significantly improved due to the reductions, and the lifespan of building materials and structures of cultural importance should lengthen. Deterioration of our historic buildings and monuments will be slowed. Finally, reductions in SO₂ and NO_x will reduce sulphates, nitrates, and ground level ozone (smog), leading to improvements in public health. The reductions in emissions will help to protect public health [69.]

There are several options for reducing SO₂ and NO_x emissions including:

- Using coal containing less sulphur;
- Washing the coal;
- Using devices called scrubbers to chemically remove the SO₂ from the gases leaving the smokestack;
- Using natural gas instead of coal (creates much less SO₂ than burning coal);
- Using catalytic converters reduce NO_x emissions from cars;
- Using alternative energy sources (nuclear power, hydropower, wind energy, geothermal energy, and solar energy);
- Alternative energies available to power automobiles (natural gas, battery-powered cars, fuel cells, and combinations of alternative and gasoline powered vehicles) [29].

This will be expensive, but the costs will be greatly outweighed by the benefits, including healthier forests and healthier people, lakes and streams full of fish, better harvests, less corrosion to buildings and cultural monuments, and less harm to the diversity of flora and

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fauna. If the correct measures are taken we will also get the added benefit of reducing emissions of carbon dioxide, the major contributor to climate change.

3.4. Heavy Metals

Heavy metals are the general term encompassing the group of metals and non-metals which density is above 6 g/cm^3 [1]. The term is commonly used for the following metals: cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb) and zinc (Zn). The alternative name for the group of elements is “trace metals” [1].

Heavy metals are naturally present in rocks and ores and that is why they always occur in soils, sediments, wastes and living organisms. Excessive, abnormal concentration of heavy metals in particular media leads to contamination [1].

Heavy metals in surface water can be from natural or anthropogenic sources (Table 3.6). Currently, anthropogenic inputs of metals exceed natural inputs (Table 3.7) [72]. Contamination of the environment occurs mainly as a result of human activities, like [1]:

- Mining of metal ores (storage of wastes, weathering of metals ores in closed mines, leakages);
- Agriculture (mineral fertilizers, pesticides, drying substances, preservatives, wastes from swine and poultry breeding, compost and manure, sewage, corrosion of metal objects);
- Combustion of fossil fuels;
- Metallurgy (specialist alloys and steels);
- Electronics (production of semiconductors and other electronic elements, sewage, corrosion of defective electronic elements);
- Chemical industry (sewage, accidental leakages);
- Pigments and paints (sewage, antifouling paints, weathering of pigments and paints);
- Storage of wastes (leakages, atmospheric precipitation, corrosion of wastes in damp pits).

All heavy metals exist in surface waters in colloidal, particulate, and dissolved phases, although dissolved concentrations are generally low. The colloidal and particulate metal may be found bounded into hydroxides, oxides, silicates, or sulphides; or adsorbed to clay, silica, or organic matter. The soluble forms are generally ions or unionized organometallic complexes.

Table 3.6. Sources of heavy metals in natural waters [10].

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Sources of heavy metals		
Nonpoint source		Point sources
Natural	Anthropogenic	Anthropogenic
Chemical and physical weathering of igneous and metamorphic rocks and soils often release heavy metals into the sediment and into the air. Other contributions include decomposition of plant and animal detritus, precipitation or atmospheric deposition of airborne particles from volcanic activity, wind erosion, forest fire smoke, plant exudates, and oceanic spray.	Surface runoff from mining operations usually has a low pH and contains high levels of metals such as iron, manganese, zinc, copper, nickel and cobalt. The combustion of fossil fuels pollutes the atmosphere with metal particulates that eventually settle to the land surface. Urban storm-water runoff often contains metals from roadways and atmospheric fallout. Currently, anthropogenic inputs of metals exceed natural inputs.	Domestic wastewater effluent contains metals from metabolic wastes, corrosion of water pipes, and consumer products. Industrial effluents and waste sludge may substantially contribute to metal loading.

Table 3.7. Global emission estimates for arsenic, cadmium, mercury, lead, and zinc at the beginning of the 1980s (after Nriagu and Pacyna. 1988).

	Source category	As	Cd	Hg	Pb	Zn
1.	Fossil fuel combustion	0.4 - 3.7	0.2 - 1.1	0.6 - 3.5	2.7 - 18.4	3.1 - 23.4
2.	Gasoline combustion	-	-	-	248.0	-
3.	Non-ferrous metal industry	9.6 - 15.1	2.6 - 8.2	0 - 0.2	30.0 - 69.6	51.0 - 93.8
4.	Other anthropogenic sources	2.0 - 6.8	0.3 - 2.7	0.3 - 2.5	8.0 - 40.0	15.9 - 76.3
A.	Total anthropogenic emissions mean values	12.0-25.6 18.8	3.1-12.0 7.6	0.9-6.2 3.6	288.7-376.0 332.0	70.0-193.5 132.0
B.	Natural emissions	7.8	1.0	6.0	19.0	4.0

The behaviour of metals in natural waters is a function of the substrate sediment composition, the suspended sediment composition, and the water chemistry. Sediment composed of fine sand and silt will generally have high levels of adsorbed metal. Metals also have a high affinity for humic acids, organo-clays, and oxides coated with organic matter. The water chemistry of the system controls the rate of adsorption and desorption of metals to and from sediment. Adsorption removes the metal from the water column and stores the metal in the substrate. Desorption returns the metal to the water column, where recirculation and bioassimilation may take place. Metals may be desorbed from the sediment if the water experiences increases in salinity, decreases in redox potential, or decreases in pH:

- Salinity increase - elevated salt concentrations create increased competition between cations and metals for binding sites; often, metals will be driven off into the overlying water.
- Redox potential decrease - a decreased redox potential, as is often seen under oxygen

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deficient conditions, will change the composition of metal complexes and release the metal ions into the overlying water.

- pH decrease - a lower pH increases the competition between metal and hydrogen ions for binding sites; a decrease in pH may also dissolve metal-carbonate complexes, releasing free metal ions into the water column.

3.4.1. Biochemical properties of heavy metals

The majority of living organisms require trace amounts of some heavy metals (they are called *microelements*). Excessive levels of essential metals, however, can be detrimental to the organisms. Trace metals which are undoubtedly necessary for health of animals and plants are copper, manganese, iron, cobalt, and zinc; cobalt, chromium, selenium and iodine for animals; boron and molybdenum for plants. Most of microelements are components of enzymes and other proteins which are important for metabolic processes.

Aquatic organisms may be adversely affected by heavy metals in the environment. Organisms are able to tolerate slight fluctuations in concentration of most of the elements [1], however elevated metal levels in natural waters may cause the following sublethal effects in aquatic organisms:

- Histological or morphological change in tissues;
- Changes in physiology, such as suppression of growth and development, poor swimming performance, changes in circulation;
- Change in biochemistry, such as enzyme activity and blood chemistry;
- Change in behaviour;
- And changes in reproduction.

Many organisms are able to regulate the metal concentrations in their tissues. Fish and crustacea can excrete essential metals, such as copper, zinc, and iron, which are present in excess. Some can also excrete non-essential metals, such as mercury and cadmium, although this is usually met with less success.

3.4.2. Environmental Fate and Transport in Water

Heavy metals introduced into environment can undergo different processes.

Water can transport metals that are bound to sediment particles, as well as dissolved metals. Although dissolved metals are primarily transported in overland flow, some underground

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transport is also possible. Metals that are introduced into the unsaturated zone and the saturated zone will most likely not be transported a long distance. Dissolved metals that are carried below the land surface will readily sorb to soil particles or lithic material in the unsaturated zone and the saturated zone [72].

Atmospheric dust containing heavy metals, falling directly into surface waters or flowing with run-off, reacts with substances present in water or deposit on the bottom, where metals react with sediments. Solubility of metal compounds depends on concentration of anions and ligands in water, water pH and its redox properties, as well as the presence of adsorbing sediments. Some metal ions are adsorbed and precipitate with hydrated oxides of Fe, Mn and Al, occurring in sediments and soils. Lots of metals precipitate also in presence of CaCO_3 , i.e. V, Mn, Fe, Co and Cd. Clay particles from sediments and soils adsorb and precipitate with V, Ni, Co, Cr, Zn, Cu, Pb, Ti, Mn and Fe [1].

Heavy metals accumulate mostly in sediments, and the content of accumulated heavy metals increases with the proportion of organic matter. Release of heavy metals from sediments is controlled by pH and the rate of organic matter decomposition [11].

To a considerable degree heavy metals accumulate also in marine invertebrates. Their concentration in organism's tissues can be many times higher than that observed in marine water, the organisms live in. Predispositions to accumulate heavy metals depend mainly on the species [1] and on the physical and chemical characteristics of the metal. Metals may enter the systems of aquatic organisms via three main pathways:

- Free metal ions that are absorbed through respiratory surface (e.g., gills) are readily diffused into the blood stream;
- Free metal ions that are adsorbed onto body surfaces are passively diffused into the blood stream;
- Metals that are sorbed onto food and particulates may be ingested, as well as free ions ingested with water.

Most of the heavy metals have a tremendous affinity for sulphur and attack sulphur bonds in enzymes, thus immobilizing the enzymes. Protein carboxylic acid ($-\text{CO}_2\text{H}$) and amino ($-\text{NH}_2$) groups are also chemically bound by heavy metals. Cadmium, copper, lead and mercury ions bind to cell membranes, hindering transport processes through the cell wall. Heavy metals may also precipitate phosphate biocompounds or catalyze their decomposition [3].

In comparison to invertebrates, aquatic plants are equally or less sensitive to cadmium,

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copper, lead, mercury, nickel, and zinc. Metal uptake rates will vary according to the organism and the metal in question. Phytoplankton and zooplankton often assimilate available metals quickly because of their high surface area to volume ratio.

Contamination with heavy metals affects the whole environment but the longest lasting effects ensue in soils. It is due to the facts that many metals absorb on humus and clay colloids, and stay in atomic form (do not decompose). Long duration of contamination in many cases can reach few hundreds or even few thousands years, depending on soil type and its physicochemical properties [1].

Heavy metals are accumulated by plants. The ability to accumulate metals is described by diffusion coefficient (concentration of a metal in overhead part of a plant divided by total concentration of a particular metal in soil), calculated for root assimilation. Assimilation of metal can be influenced by soil pH, organic matter content and plant genotype, and can also take place in leaves due to atmospheric precipitation [1].

The comparison of heavy metals concentration in polluted and clean environment is presented in Table 3.8.

Table 3.8. Heavy metals content in plants in Poland.

Plant	Natural Environment				Polluted Environment			
	Zn	Cr	Pb	Cd	Zn	Cr	Pb	Cd
Wheat	-	0.5	-	0.3	-	-	10	10
Rye	14	0.2	0.5	-	170	-	-	-
Potato	25	-	1.2	0.2	90	-	16	0.5
Lettuce	100	-	2.0	-	1000	-	234	-
Carrot	70	-	-	-	320	-	-	-
Grass	-	0.7	2	0.5	-	44	65	32
Tomato	-	0.6	0.7	-	-	3	10	16

Heavy metals in the environment can undergo *methylation*. As, Hg, Se, Te, Pb and Tl undergo methylation as a result of activity of enzymes secreted by microorganisms (so called biomethylation) and also due to nonbiological chemical reactions. It seems that Cd, In, Sb and Bi can be methylated as well. Bacteria taking part in these reactions were found in river and lake sediments, sea coastal sediments, soils and alimentary canal of animals and humans. Methylation significantly influences behaviour of metals in environment, their biological availability and toxicology [1].

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3.4.4. Characteristics of Heavy Metals

Non-essential heavy metals of particular concern to surface water systems are arsenic, cadmium, chromium, lead, mercury, and selenium.

a. Arsenic (As)

The most significant water pollutant metalloid element is arsenic, a toxic element that has been the chemical villain of more than a few murder plots [3]. Arsenic is naturally present in waters due to weathering of rocks and soil containing phosphate minerals; however anthropogenic sources contribute to considerable contamination of the environment. Uses of arsenic include:

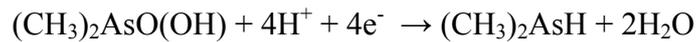
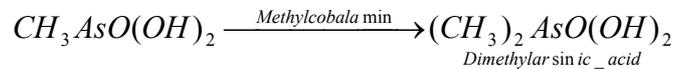
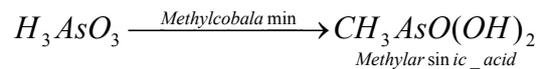
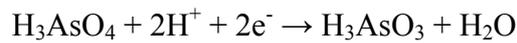
- Paint pigments, textile dyeing and calico printing;
- Pharmaceuticals (used for its medicinal virtues in the form of organic arsenicals);
- Pesticides (particularly those used before World War II, insecticides and rodenticides);
- Wood preservatives;
- Poultry and swine feed additives;
- Combustion of fossil fuels (fossil fuel combustion, particularly coal, introduces large quantities of arsenic into the environment, much of it reaching natural waters [3]; Coal burning has contributed ~ 290 000 metric tons of arsenic in the last 70 years [17]);
- Detergents (several common presoaks and household detergents were shown to contain 10 - 70 mg/ kg of arsenic);
- Mine tailings and smelting (by-product of copper, gold, and lead refining greatly exceeds the commercial demand for arsenic, and it accumulates as waste material [3]);
- Lead alloys for bullets and shot, pyrotechnic and boiler compositions;
- Depilatory agent;
- Opal glass and enamels (bronzing agent or decolorizing agent for glass).

Most anthropogenic inputs reach rivers, lakes and oceans. The total arsenic content of the world's oceans is approximately $2.8 \cdot 10^9$ metric tons. The sum of all anthropogenic contributions is estimated to be 110 000 tons per year for this century. This is approximately 2.5 times the contribution due to weathering [17].

Arsenic species, As^{+5} , As^{+3} and methylated As, occur in natural waters. Arsenic is a good tracer for geochemical and biological processes and for rare-element transportational pathways. It forms a variety of inorganic and organic compounds of different toxicity to

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aquatic organisms. This is due to the varying physico-chemical properties of the arsenicals in different valency states. Arsenic compounds in the environment are vulnerable to chemical and biological transformations [17]. Arsenic may be converted to more mobile and toxic methyl derivatives by bacteria, according to the following reactions [3]:



The conservative behaviour of arsenic in surface waters is altered by organic complexation which reduces surface interactions with solid phase components of the water column. Arsenic also binds to particulate matter and the association is reported to be non-labile, with no significant exchange to the dissolved phase. Moreover, the particulate load could deposit entirely in estuaries and coastal zones delivering only the dissolved fraction to the ocean.

Relatively high levels of arsenic are found in freshwater sediments. Sediments from a warm, shallow lake contained <0.5 to 59 mg As per kg with an average of 22 mg/ kg. Concentrations were positively correlated with decreasing particle size of the sediment [17].

Arsenic ingestion can cause severe toxicity through ingestion of contaminated food and water. Toxicological importance of arsenic is connected with its similarity to phosphorous. This brings about metabolic chains being broken by arsenic [1]. Arsenic ingestion causes vomiting, diarrhoea, and cardiac abnormalities [17]. Acute arsenic poisoning can result from the ingestion of more than about 100 mg of the element. Chronic poisoning occurs with the ingestion of small amounts of arsenic over a long period of time. There is some evidence that this element is also carcinogenic [3].

In the last five years, environmental restrictions and regulations have limited the amount of arsenic produced and used [17]. In 1999, the National Academy of Sciences concluded that the current standard of 50 ppb does not sufficiently protect public health [60]. The

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Environmental Protection Agency wants to reduce the limit for arsenic allowed in drinking water to 5 ppb [61].

b. Cadmium (Cd)

Cadmium is natural constituent of surface waters and groundwater, found in the Cd^{+2} oxidation state. It may exist in water as the hydrated ion, as inorganic complexes such as carbonates, hydroxides, chlorides or sulphates, or as organic complexes with humic acids [62]. Pollutant cadmium in water may arise from industrial discharges (direct discharge from industrial operations - metal processing operations) and mining waters, weathering and erosion of soils and bedrock, atmospheric deposition, leakage from landfills and contaminated sites (phosphate fertilizers), dispersive use of sludge and fertilizers in agriculture and burning of fossil fuels [3].

Cadmium and its compound have found increasing applications in a variety of industrial products and operations. The main are the following:

- Electroplating - cadmium is deposited either electrolytically or mechanically on objects to provide bright appearance and resistance to corrosion; cadmium is also used in the packing industries except food packing;
- Pigments - cadmium pigments are used in the plastic industry, ceramics, paints, and coatings; cadmium pigments are used in traffic paints, high quality industrial finishes, and in the glass enamel red label on 'Coca-Cola' bottles;
- Plastic stabilizers - cadmium stearates are used as stabilizers in the production of polyvinyl chloride plastics (PVC);
- Batteries - due to its perfectly reversible electrochemical reactions at a wide range of temperature, low rate of self discharge, and easy recovery from dead batteries, cadmium is employed extensively in batteries.

Other uses of cadmium are: (i) cadmium phosphors as tubes in television sets, fluorescent lamps, x-ray screens, cathode-ray tubes, and phosphorescent tapes, (ii) cadmium alloys in Cd-Ag solders, automatic sprinkler systems, fire-detection apparatus, valve seals for high-pressure gas containers, trolley and telephone wires, and in automobile radiator finstock, (iii) electrical and electronic applications such as heavy duty relays, switches, automobile distributor contacts, and solar and photocells [17].

Worldwide annual emissions of cadmium from natural sources are approximately $8.43 \cdot 10^5$ kg. Vegetation, airborne soil particles, volcanogenic aerosols, and forest fires contribute to

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natural emissions. The annual atmospheric input from industrial activities accounts for $7.19 \cdot 10^6$ kg. Precipitation removes cadmium effectively from the atmosphere. Hence concentrations in rainwater may exceed $\geq 50 \mu\text{g}/\text{dm}^3$ [17].

Dissolved cadmium levels in freshwater generally range from 10 to $500 \text{ ng}/\text{dm}^3$. However, in cases of extreme pollution, concentrations may exceed $17\,000 \text{ ng}/\text{dm}^3$. Oceanic waters show significant enrichment (up to $125 \text{ ng}/\text{dm}^3$) at mid-depth. It has been suggested that aquatic organisms incorporate Cd in their tissue and transport it to deeper waters through sinking of their detritus and debris [17].

Much of the cadmium entering fresh waters from industrial sources may be rapidly adsorbed by particulate matter, and thus sediment may be a significant sink for cadmium emitted to the aquatic environment [62].

Cadmium is highly toxic element, not essential for normal functioning of organism. It has high lipid solubility and bioaccumulation, and accumulates primarily in major organ of animal tissues rather than in muscle. Cadmium accumulates in kidneys leading to serious disorders [1].

The effects of acute cadmium poisoning in humans are very serious, high blood pressure, kidney damage, destruction of testicular tissue, and destruction of red blood cells among them [3]. High concentration in inhaled air can cause emphysema and severe inflammatory [1]. There are few recorded instances of cadmium poisoning in humans following consumption of contaminated fish or water. Because cadmium accumulates in organs and has long half-life (10-30 years), the ingestion of small amounts of contaminated fish over long periods may lead to some form of cadmium intoxication [17].

c. Chromium (Cr)

Chromium is a naturally occurring element found in rocks, animals, plants, soil, and in volcanic dust and gases. There are two forms of chromium species that may be present in water: chromium Cr^{+3} and chromium Cr^{+6} .

Chromium enters environmental waters mainly from anthropogenic sources [65]:

- Electroplating factories;
- Leather tanneries and textile manufacturing facilities;
- Wood treatment;
- Burning coal and oil;

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- Steel production and stainless steel welding.

The three major industrial uses are metallurgical, refractory and chemical [39].

Chromium (III) is an essential (exogenous) microelement, crucial for hydrocarbons metabolism in animals [1]. Toxicity of chromium to aquatic organisms is generally low. Under most conditions, mercury, cadmium, copper, lead, nickel, and zinc are more toxic than chromium. Toxicity to plants depends on pH of the media and hence the availability of free and chelated ions. Other factors, such as presence of organic chelators, cations, nutrients, and other heavy metals in solution likely influence toxicity to plants [17].

Chromium is not acutely toxic to humans. The chronic adverse health effects are respiratory and dermatologic [17]. However, in case of chronic exposure to chromium-containing dusts the element can be carcinogenic (respiratory system) [1].

d. Copper (Cu)

Copper and its compounds are widely distributed in nature including surface waters and some groundwater. It is present in form of dissolved or insoluble compounds. In waters with high concentration of hydrocarbons copper occurs as Cu^{2+} ions and in form of complexes CuCO_3 , $[\text{Cu}(\text{HCO}_3)_2]$, $[\text{Cu}(\text{OH})_3]^-$ and $[\text{Cu}(\text{OH})_4]^{2-}$. It also forms complexes with silicates, sulphates, nitrates and phosphates. Among organic compounds there are Cu-complexes with aminoacids, polypeptides, and humic substances [6].

Contamination with copper can originate mainly from the following sources:

- Mining and metallurgy (industrial sewage);
- Production of Cu-containing alloys (brass);
- Galvanization;
- Corrosion of wires and devices made of copper, brass or bronze;
- Excessive use of Cu-containing pesticides.

Copper sulphate is widely used as anti-algae agent in decorative ponds and even in drinking water reservoirs attacked by booming Cyanophyceae algae. Copper is also used in households for waterwork-fittings.

Copper is an essential microelement in the human metabolism. Daily demand of an adult is equal to 5 mg Cu. Higher concentrations of copper are harmful for health. Because copper do not accumulate in organism so easily like i.e. lead or mercury, it is established that harmful daily dose can be as high as 100 mg [6].

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Copper in concentration above 1 mg/dm³ may be toxic for fish and restrain vegetation growth. Copper toxicity is pH depending, the higher pH the higher toxicity [2].

e. Lead (Pb)

Lead is a naturally occurring metal found in small amounts in the earth's crust. It is a trace metal that is present naturally in soils and water in trace amounts. It has no characteristic taste or smell. Metallic lead does not dissolve in water but can combine with other chemicals to form lead compounds or lead salts (occurs in water in the Pb⁺² oxidation state). This depends on the acidity and temperature of the water (Table 3.9).

Table 3.9. Solubility of lead and lead compounds.

Element / Compound	Solubility in Water	Solubility in Organic solvents
Lead	Insoluble	Insoluble
Lead acetate	221g/100ml at 50°C	Soluble in glycerol, very slight in alcohols
Lead chloride	0.99 g/100ml at 20°C	Insoluble in alcohol
Lead chromate	0.2 mg/l	Insoluble in acetic acid
Lead nitrate	37.65-56.5 g/100ml at 0°C	1 g in 2,500 ml absolute alcohol 1 g in 75 ml absolute methanol
Lead oxide	0.0023 g/100 at 23°C	Soluble in alkali chlorides
Lead sulphate	42.5 mg/l at 25°C	Insoluble in alcohol

Human activities have spread lead and substances that contain lead to all parts of the environment. Increased amounts of lead are due to atmospheric pollution caused by burning of fossil fuels, smelting, traffic, use of paints, waste incineration, pesticides, and agricultural application of sewage. Sources of lead in natural waters include deposits of lead-containing dust from the atmosphere, waste water from industries (primarily iron and steel industries and lead producers), urban runoff and mining piles [65]. Comparison of lead emission, also with other metals, is presented in Table 3.10.

Lead is one of the oldest metals known to man and, since medieval times, has been used in piping, building materials, solders, paint, type metal, ammunition, and castings. In more recent times lead has been used mainly in storage batteries, metal products, chemicals, and pigments.

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- Storage batteries - lead is mainly used in acid storage batteries; significant improvements have been made to reduce the unit lead weight in a battery and also to increase the average battery life and performance;
- Metal products - two most important products are ammunition and solder followed by casting materials, sheet lead, and others; it is also used in the mounting of various types of equipment including air-conditioning systems, heavy industrial equipment, and commercial laundry machines; additional applications include cable sheathing, collapsible tubes, caulking materials, and corrosive-liquid containers;
- Chemicals - tetraethyllead constitutes an antiknock agent in gasoline; lead stearate is used in the production of synthetic polymers;
- Pigments - the use of lead in anticorrosive and highway traffic safety paints.

Other uses of lead include automotive wheel weights, ship ballast, and various alloys, and as lead-ferrite for permanent magnets in small electric motors [17].

Lead from leaded gasoline used to be a major source of atmospheric and terrestrial lead, much of which eventually entered natural water systems. In addition to pollutant sources, lead-bearing limestone and galena (PbS) contribute lead to natural waters in some locations [3].

Table 3.10. Estimated global atmospheric lead emission.

Source Category	Emission (metric tons per year)	Percentage of total
Oil and gasoline combustion	273 000	60.8
Coal combustion	14 000	3.1
Waste incineration	8 900	2.0
Wood combustion	4 500	1.0
Iron and steel production	50 000	11.1
Secondary non-ferrous metal production	770	0.2
Primary copper smelting	27 000	6.0
Mining non-ferrous metals	8 200	1.8
Primary lead smelting	31 000	6.9
Primary zinc smelting	16 000	3.5
Primary nickel smelting	2 500	0.5
Industrial applications	7 400	1.6
Miscellaneous	5 950	1.3
TOTAL	449 200	100%

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On the basis of comparison with other metals it can be affirmed that lead is neither the most toxic nor the most easily biologically available, yet it occurs in the greatest number of media, and moreover, accumulates in animals' organisms.

In case of plants high residues are often reported for plants inhabiting polluted waters. Estuarine and coastal marine species generally contain lower residues than those reported for freshwater plants. The relatively low lead content of marine species is primarily related to the extent of ambient lead pollution in coastal waters. Because there is often a good correlation between lead levels in water and plant tissues, several major species have been used as biomonitors of environmental contamination. These include freshwater representatives of *Eloдея*, *Cladophora* and *Myriophyllum*, and estuarine *Fucus*, *Laminaria* and *Ascophyllum*. The use of such species partially overcomes variability in the concentrations of lead in water [17].

In case of humans toxic concentration of lead can occur in bone marrow, where blood cells are produced. Lead can influence the process of haemoglobin production, and that is why lead poisoning causes anaemia. The victim of mild poisoning may have headaches and sore muscles and may feel generally fatigued and irritable [1].

Because of size and charge similarities, lead can substitute for calcium and included in bone. Children are especially susceptible to lead because developing skeletal systems require high calcium levels. Lead that is stored in bone is not harmful, but if high levels of calcium are ingested later, the lead in the bone may be replaced by calcium and mobilized.

Acute lead poisoning in humans causes severe dysfunction in the kidneys, reproductive system, liver, and the brain and central nervous system, as lead is a strong neurotoxin [1]. Despite greatly increased total use of lead by industry, evidence from hair samples and other sources indicates that body burdens of this toxic metal have decreased during recent decades. This may be the result of less lead use in plumbing and other products that come in contact with food or drink [3].

Lead is probably not a major problem in drinking water, although the potential exists in cases where old lead pipe is still in use. Lead used to be a constituent of solder and some pipe-joint formulations, so that household water does have some contact with lead. Water that has stood in household plumbing for some time may accumulate spectacular levels of lead (along with zinc, cadmium, and copper) and should be let run for a while before use [3].

f. Mercury (Hg)

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Mercury is a natural metallic element, known to the ancient Chinese, Hindus and Egyptians. Shiny, silver-white and mirrorlike, it is the only common metal existing as a liquid at ordinary temperatures. It is slightly volatile at ordinary temperatures and solidifies at -39° forming a tin-white, ductile, malleable mass which may be cut with a knife. Mercury forms alloys with most metals except iron and combines with sulphur at ordinary temperature.

Mercury is one of the most toxic metals, even more so than lead. It is the most concern of any of the heavy-metal pollutants. Mercury is a naturally occurring metal found throughout the environment as a result of normal breakdown of the earth's crust (minerals). The total amount of mercury in the environment caused by natural processes throughout the world is far greater than the total amount caused by human activities. However, the amount of mercury that exists in any one place through natural processes is usually very low. In contrast, the amount of mercury that may be at a particular waste site because of human activity can be very high [65].

The anthropogenic sources of mercury and the common areas where mercury is found are:

- Water treatment facilities
- Plumbing - piping
- Batteries
- Broken thermometers
- Barometers
- Discarded laboratory chemicals
- Pesticides
- Fertilizers
- Fungicides
- Pharmaceutical products
- Amalgam tooth fillings
- Laxatives
- Disposal of wastes
- Tanning weather
- Mercury-vapour lamps
- Wood preservatives
- Auto exhaust
- Air conditioner filters
- Adhesives
- Cosmetics: mascara
- Calomel (talc, body powder)
- Drinking water (tap and well)
- Bleached flour
- Processed foods
- Cinnabar (used in jewellery)
- Floor waxes and polishes
- Electric switches
- Paint pigments
- Fabric softeners
- Releases of water containing mercury from factories

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Taken individually, each of these sources may not contribute much of the toxic metal, but the total effect can be substantial. Figures and trends for worldwide mercury discharges proven that [17]:

- Most of the increases in mercury discharge into the environment occur in the less developed regions of the world;
- In the developed regions of the world, discharges into water are either increasing very little or show a real decline;
- Air discharges through human activities will double between 1975 and 2025, though they might constitute only 25% of natural air discharges.

Mercury during circulation in the environment (Fig. 3.11) undergoes many significant transformations:

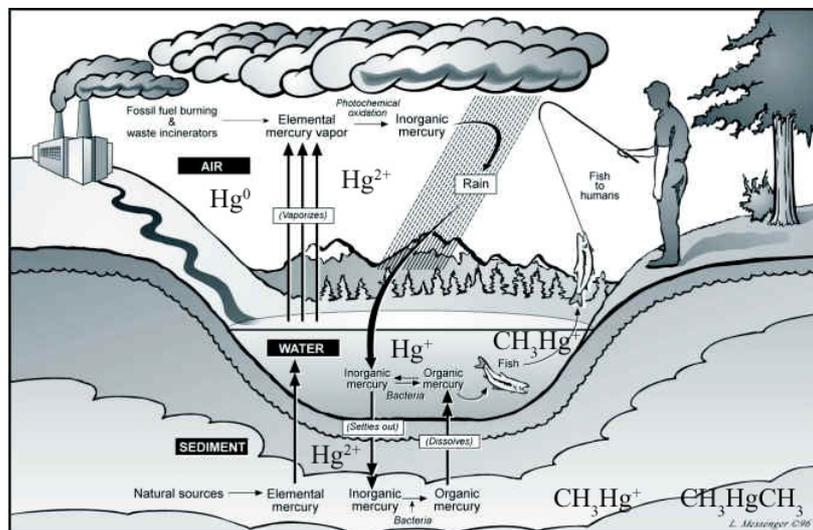
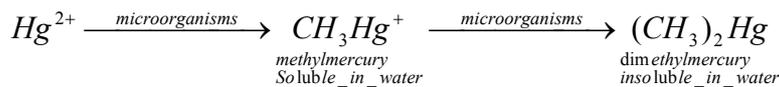
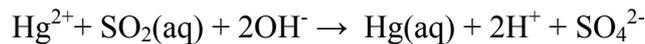
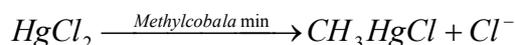


Fig.3.11. Circulation of mercury (Hg) in the environment.

Unexpectedly high concentrations of mercury found in water and in fish tissues in the U.S. and Canada around 1970 were later attributed to the formation of soluble monomethylmercury ion, CH_3Hg^+ , and volatile dimethylmercury, $(\text{CH}_3)_2\text{Hg}$, by anaerobic bacteria in sediments. Mercury from these compounds becomes concentrated in fish fatty

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tissue. The methylating agent by which inorganic mercury is converted to methylmercury compounds is methylcobalamin, a vitamin B₁₂ analog:



It is believed that the bacteria that synthesize methane produce methylcobalamin as an intermediate in the synthesis. Thus, waters and sediments in which anaerobic decay is occurring provide the conditions under which methylmercury production takes place. In neutral or alkaline waters, the formation of dimethyl mercury, (CH₃)₂Hg, is favored. This volatile compound can escape to the atmosphere [3].

Mercury is a toxic persistent, bioaccumulative pollutant. Methyl mercury is a chemical species that bioaccumulates in fish [33], and the only heavy metal that can bioaccumulate in organisms along the food chain [1]. Both forms of mercury, divalent mercury Hg²⁺ and organometallic compound Hg(CH₃)₂, are very toxic. Among the more severe toxicological effects of mercury are neurological damage (permanently damages brain), including irritability, paralysis, blindness, or insanity, chromosome crack, and birth defects (permanent harm to unborn children). Mercury may cause cancer, damages the stomach and large intestine, lung damage, increased blood pressure and heart rate. It permanently damages kidneys [33].

The toxicity of mercury was tragically illustrated in the Minamata Bay area of Japan⁴ during the period 1953-1960 [17].

To protect people from the possible health effects of exposure to mercury the Environmental Protection Agency (EPA) has limited the level of inorganic mercury in rivers, lakes, and streams to 144 ng/dm³ (144 parts per trillion (ppt)). EPA estimates that for an adult of average weight, exposure to 0.021 milligrams of inorganic or organic mercury per day in food or water will probably not result in any harm to health [33].

g. Zinc (Zn)

⁴ See information on Minamata disaster on:
<http://www1.umn.edu/ships/ethics/minamata.htm>
<http://www.american.edu/TED/MINAMATA.HTM>
<http://www.jinjapan.org/access/pollution/minamata.html>

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Zinc is a rather common element present in the environment. In water it occurs as Zn^{2+} cation, in form of soluble organic and inorganic complexes, or insoluble form – as hydroxides, sulphates and carbonates [6].

Zinc is naturally present in earth's crust, in form of ores. It penetrates into groundwater from soil placed close to deposits of zinc ores or other deposits rich in zinc compounds. In surface waters zinc is usually of anthropogenic origin. Zinc gets to surface waters with dust pollutants and industrial sewage (metallurgy and chemical industry). Zinc compounds are, among other things, used in [6];

- Production of zinc-paints;
- Dyeing;
- Textile printing;
- Leather and textile preservation;
- Anti-mould specimens;
- Disinfection agents;
- Wood preservatives.

Contamination with zinc is strictly connected with its mining and smelting [1].

Relatively widespread source of Zn in the environments is galvanized steel. Zinc is gradually dissolved or washed away from wire fences of roofs, eventually reaching soils and water. Sewage disposal and use of manure is also a significant source of Zn in soils and water [1].

Zinc can be present in water, especially in drinking water, as a result of metals corrosion – pipes and galvanised devices [6].

Zinc is a microelement essential in human organism. Its deficiency leads to disorders in organism's functioning, eventually resulting in growth inhibition and delayed sexual maturity. From an environmental point of view Zn is mainly toxic for plants, while slightly toxic to animals and humans [1].

3.5. Metals Speciation

In the centre of interest of all environmental sciences lies the question about the relationship between the forms, properties and quantities of specific physical and chemical forms of an element in the environment and the effects of these forms on the biota and geochemical cycles. The toxicity, bioavailability, bioaccumulation, biodegradability, persistence, mobility,

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solubility, extractability and many other critical properties depend on the form and nature of the chemical species [12]. Speciation analysis or simply speciation is in fact the determination of these distinct species.

According to the official definition of the International Union of Pure and Applied Chemistry (IUPAC) „*Speciation analysis is the process leading to the identification and determination of different chemical and physical forms of an element existing in a sample*”.

Although this definition tends to restrict the term speciation to the state of distribution of an element among different chemical species in a sample, in practice the use of this term is much wider, specifying either the transformation and/or the distribution of species, or the analytical activity to identify chemical species and measure their distribution.

The term speciation encompasses usually two slightly different connotations of speciation: the functional one and the operational one:

- Functionally we may identify and distinguish between species that are, for example, available to plants or ecotoxic; species of an element that are more easily exchangeable in mineral surfaces than others, etc [12].
- Operationally speciation is determined by the physicochemical properties of the real natural entities which are the so called species and from the analytical techniques and means which are available to the researchers to determine them [12].

So, speciation refers, basically, to the determination of the concentration of various fractions, which are clusters of species which having different physicochemical properties and such as are extractable or detectable under specific conditions and with specific means [12].

Table 3.11. Different types of speciation analysis and their application.

Type of speciation analysis	Area of application	Remarks	Examples
Physical speciation			
	environmental pollution analyses (air, water, soil)	chemical processes investigations and biochemical processes undergoing in different elements of environment	trace metals analysis (soluble and suspended fraction); trace metals analysis of different forms present in soil and sediment after sequential extraction
Chemical speciation			
screening speciation	environmental pollution analyses food pollution analyses ecotoxicology	s the simplest case of speciation analysis, which leads to the detection and determination of one definite analyte	determination of tributyltin in sea water, sediments, tissue; determination of methylmercury in tissue;
group	environmental	This case of speciation analysis leads	determination of chromium

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speciation	pollution analyses food pollution analyses ecotoxicology	to the determination of the concentration level of the specific group of compounds or elements existing in different compounds and forms and at the specific oxidation level	compounds (Cr(VI)); determination of organic matter in samples by the assignation of summary parameters (i.e. TOC in water or TH in air); level determination of concentration of different forms of mercury (elementary, inorganic and organic);
distribution speciation	environmental pollution analyses ecotoxicology	This type of speciation is connected in most cases with the analyses of biological samples.	determination of trace metals in blood serum and blood cells; determination of heavy metals in plants;
individual speciation	environmental pollution analyses food pollution analyses ecotoxicology	The most difficult form of speciation analysis. Fractionation and separation techniques have played a particular role. Unique application of chromatography and coupled techniques in this area of speciation analysis.	identification and determination of chemical species defined as to molecular, complex, electronic or nuclear structure

Different types of speciation analysis as well as the main area of their application are listed in Table 3.11 and 3.12. Generally speciation analysis plays a unique role in:

- Studies of biogeochemical cycles of chemical compounds;
- Determination of toxicity and ecotoxicity of selected elements;
- Quality control of food products;
- Control of medicines and pharmaceutical products;
- Technological process control;
- Research on the impact of technological installation on the environment;
- Examination of occupational exposure;
- Clinical analysis.

The harmful effects of the chemical forms of metallic pollutants are observed during monitoring of different environmental compartments - air, natural waters, soil, sediments, biota. The examples of monitoring are determination of organolead in leaded gasoline, determination of organotin emitted from the antifouling paints, discrimination between ionic mercury and methylmercury in environmental, clinical, and foodstuff samples. Contamination of food products (e.g. oysters and mussels by organotin, fish by methylmercury, and wine by lead compounds) is the most prominent area of speciation.

Table 3.12. Main application areas of speciation analysis.

Element	Application area of speciation analysis
Aluminium (Al)	• polymerisation products;

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	<ul style="list-style-type: none"> • forms of aluminium (e.g. labile, complexed) in serum; • forms of aluminium in food products
Antimony (Sb)	<ul style="list-style-type: none"> • redox forms and organoantimony compounds in the environment and food products
Arsenic (As)	<ul style="list-style-type: none"> • redox forms and organoarsenic compounds in the environment • arsenic-bound proteins in serum and hemoglobin • arsenic in food products • forms of arsine AsH_3 (arsenous hydride) in indoor air at work-place
Cadmium (Cd)	<ul style="list-style-type: none"> • complex-organic cadmium compounds, metallothione
Chromium (Cr)	<ul style="list-style-type: none"> • redox forms of chromium [Cr(VI)] in the environment • chemical forms of chromium coupled with proteins
Iodine (I)	<ul style="list-style-type: none"> • iodine forms in the environment and biological fluids
Lead (Pb)	<ul style="list-style-type: none"> • forms of lead compounds in the environment, e.g. trialkylated Pb compounds
Phosphorus (P)	- phosphine (hydrogen phosphides) in indoor air at work-place
Mercury (Hg)	<ul style="list-style-type: none"> • forms of mercury compounds in the environment and food products (in particular methylmercury)
Platinum (Pt)	<ul style="list-style-type: none"> • inorganic forms in the environment • metalloorganic forms of cis-platinum in medicine (therapeutic)
Selenium (Se)	<ul style="list-style-type: none"> • inorganic and organometallic selenium compounds in the environment and food products
Tin (Sn)	<ul style="list-style-type: none"> • organometallic forms in the environment and food products (e.g. shellfish)
Actinide Series	<ul style="list-style-type: none"> • chemical forms of compounds in the environment and in radioactive waste storage places

Speciation analysis requires a multi-step approach, typically including the following operations [66]:

- Sampling and storage - these are often the weakest links in the analytical chain; in speciation analysis, removal of the sample from its' natural surroundings may induce pronounced chemical and physical changes causing the species distribution to alter;
- Sample preparation and work-up - e.g. gas extraction, liquid extraction, solid phase extraction, distillation, membrane extraction, supercritical fluid extraction;
- Instrumental analysis - ideally analytical methodology for speciation purposes should be such that the measurement occurs on the undisturbed material in its natural environment.

Metal speciation on the samples in their undisturbed dynamic habitat will remain wishful thinking for a long time to come. In the meantime in-situ techniques on specimens which are taken out of their natural environment into laboratory circumstances are supposedly the best approach to minimize the alterations brought along by the sampling act. It became clear from the many discussions that sampling plays the more crucial role in metal speciation work [13].

3.6. Polycyclic Aromatic Hydrocarbons (PAHs)

The term Polycyclic Aromatic Hydrocarbons, or PAHs, is used for molecules which contain at least two aromatic benzene rings in their structure [6].

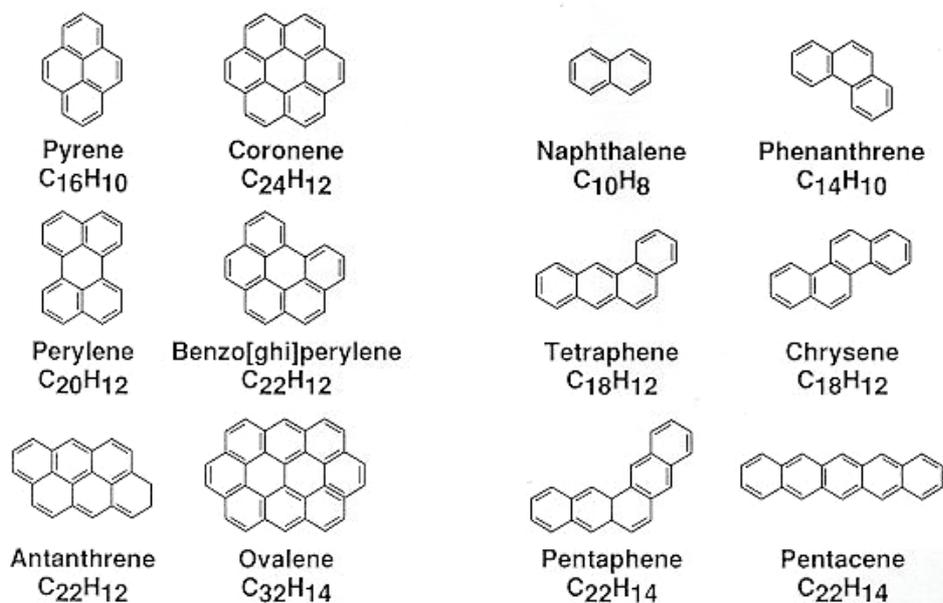


Fig. 3.12. Structures of some Polycyclic Aromatic Hydrocarbons.

PAHs are a class of very stable organic molecules made up of only carbon and hydrogen and the group consists of over 100 different chemicals. The structures of a variety of representative PAHs can be seen below, in Fig.3.12 [64].

3.6.1. Sources of PAHs

PAHs are released into the atmosphere as gases or particles during the incomplete combustion of organic materials and fossil fuels. Generally, PAHs are formed when materials burn at low temperatures [6]. Studies performed during the last decades showed that PAHs have a significant variation in their composition for different combustion sources [25].

PAHs are found in coal tar, crude oil, soot, rubber, [6] and creosote wood preservatives. Many useful products such as mothballs and blacktop contain PAHs. They are also found at low concentrations in some special-purpose skin creams and antidandruff shampoos that contain coal tars. A few are used in medicines or to make dyes, plastics, and pesticides. Automobile - Diesel and benzene - exhaust (mobile-cars, trucks, ships and aircraft), industrial emissions (industrial-power generation, steelworks, coke ovens, aluminium production,

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cement kilns, oil refining and waste incineration) and smoke from burning wood, charcoal and tobacco contain high levels of PAHs. PAHs are formed during roasting, frying and smoking of meat [6].

PAHs which enter and pollute the air are present mainly due to releases from volcanoes, forest fires, burning coal, and automobile exhaust, while PAHs enter water through different ways:

- Discharges from industrial wastes from coking plants, gas-works, petrochemical plants and others;
- Municipal wastes (sewage) very often containing admixtures of industrial wastes;
- Atmospheric precipitation containing dusts;
- With crude oil and mineral oils;
- Discharges from wastewater treatment plants;
- Due to leaching of soil, decaying plant and animal matter;
- Washing away bituminous covers of waterworks system (corrosion protection);
- From ash, tar, or creosote that is improperly disposed in landfills;
- Due to living activity of some organisms (bacteria, algae and plants metabolites).

PAHs in natural waters, therefore, can be of natural origin (minimal quantity) and artificial (sewage, atmosphere, etc.). Concentration of PAHs in surface water and sewage and treated water is presented in Tables 3.13 - 3.15.

Table 3.13. PAHs content in river water samples.

PAH	PAH content [ng/dm ³]		PAH content in suspension %
	Water sample with suspension	Water sample after suspension removal	
Fluoranten	610	12,7	97,9
Benzo[h]fluoranthene	93	1,0	98,9
Benzo[b]fluoranthene	18	0,25	98,6
Benzo[a]pyrene	352	3,0	99,2
Benzo[ghi]perylene	520	3,6	99,3

Table 3.14. PAHs content in municipal sewage.

PAH	Concentration No-rain time	PAH [ng/dm ³] After heavy rains	Multiplicity of increase
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Fluoranthene	352	16350	46
Pyrene	254	16050	63
Benzo[a]anthracene	25	10360	415
Benzo[b]fluoranthene	39	10790	254
Benzo[k]fluoranthene	22	1840	170
Benzo[a]pyrene	1	3840	3840
Benzo[ghi]perylene	4	4180	960
Indeno[1,2,3-cd]pyrene	17	4980	293
TOTAL	771	87300	about 100

Table 3.15. PAHs removal while sewage treatment.

PAH	PAH content [ng/dm ³]		
	Raw sewage	Sewage after mechanical treatment	Sewage after biological treatment
Fluoranthene	45,3	14,6	0,26
Pyrene	11,8	2,3	0,04
Benzo[a]anthracene	31,4	6,0	0,05
Benzo[b]fluoranthene	23,7	4,8	0,15
Benzo[k]fluoranthene	29,6	11,6	-
Benzo[a]pyrene	34,5	1,4	0,03
Benzo[ghi]perylene	8,7	1,2	0,03
Indeno[1,2,3-cd]pyrene	15,0	3,0	0,12
TOTAL	211,1 (100%)	44,9 (22%)	0,68

When PAHs get into surface waters they contaminate waters for longer than other organic compounds. Moreover they accumulate in the sediments. Surface waters containing PAHs can be the reason for groundwater contamination, especially if filtration layer of soil is not compact enough. Under those circumstances hydrocarbons easily soak into soil and the deeply percolate. The presence of surface active agents (detergents), which are good solvents of hydrocarbons, is conducive to the process. PAHs are extremely durable in groundwater [6].

3.6.2. Properties of PAHs

Most PAHs do not dissolve easily in water, yet they can form emulsions with water [6]. Solubilities and vapour pressures of different PAHs are listed in Table 3.16. Due to their low vapour pressure, most PAHs immediately condense and adsorb onto particulate or form very small particles themselves (average diameter 1µm) [67]. PAHs can stick to solid particles and settle to the bottoms of lakes or rivers, certain PAHs move through soil to contaminate

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underground water [64]. Polycyclic aromatic hydrocarbons are usually chemically stable and also do not decompose under the influence of microorganisms activity [6].

Table 3.16. Physico-chemical properties of PAHs.

Compound (cancerogenicity)	M.W.	Solubility in water [$\mu\text{g/l}$]	log K _{octanol-water}	Vapour pressure [mm Hg]
 benzo/b/fluoranthene (+++)	252	1,2	6,57	$5,0 \cdot 10^{-7}$
 benzo/k/fluoranthene (+++)	252	0,55	6,84	$5,0 \cdot 10^{-7}$
 benzo/a/pyrene (++++)	252	3,8	6,50	$5,0 \cdot 10^{-7}$
 indeno/1,2,3c,d/pyrene (++)	276	62,0	7,66	$1,0 \cdot 10^{-10}$
 benzo/g,h,i/perylen (++)	276	0,26	7,10	$1,0 \cdot 10^{-10}$
 dibenzo/a,h/anthracene (++)	278	0,50	7,19	$1,0 \cdot 10^{-10}$
 naphthalene	128	31700,0	3,36	$4,9 \cdot 10^{-2}$
 acenaphthene	152	3470,0	3,94	$2,0 \cdot 10^{-2}$
 acenaphthylene	154	3930,0	4,03	$2,9 \cdot 10^{-2}$
 fluorene	166	1980,0	4,47	$1,3 \cdot 10^{-2}$
 phenanthrene	178	1290,0	4,57	$6,8 \cdot 10^{-4}$
 anthracene (-)	178	73,0	4,54	$1,9 \cdot 10^{-4}$
 fluoranthene (-)	202	260,0	5,22	$6,0 \cdot 10^{-6}$
 pyrene (-)	202	135,0	5,18	$6,8 \cdot 10^{-7}$
 benzo/a/anthracene (++)	228	14,0	5,91	$5,0 \cdot 10^{-9}$
 chryzene (-)	228	2,0	5,91	$5,0 \cdot 10^{-9}$

3.6.3. PAHs fate in the environment

The environmentally significant PAHs are those molecules containing two to seven benzene rings. The low molecular weight PAHs - those containing two to three benzene rings, for example, naphthalenes, fluorenes, phenanthrenes and anthracenes - are acutely toxic to aquatic organisms, whereas the high molecular weight PAHs - those containing four to seven

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rings - are not. However, several high molecular weight PAHs are known to be carcinogenic (e.g., B[a]P) [27].

PAHs accumulate in fatty tissue of aquatic organisms, like fish or molluscs [6], and PAHs contents of plants and animals may be much higher than PAHs contents of soil or water in which they live [64].

Polycyclic aromatic hydrocarbons are carcinogenic to smaller or larger extent. On the basis of their carcinogenic effect PAHs were divided for inactive, slightly active, medium active, strongly active and very strongly active [6]. The US EPA has identified 16 priority PAHs, based on concerns that they do or might cause cancer in animals and humans. These are [31]:

- | | |
|-------------------------|--------------------------|
| 1. Acenaphthene | 9. Chrysene |
| 2. Acenaphthylene | 10. Dibenz[ah]anthracene |
| 3. Anthracene | 11. Fluoranthene |
| 4. Benz[a]anthracene | 12. Fluorene |
| 5. Benzo[a]pyrene | 13. Indeno[123-cd]pyrene |
| 6. Benzo[b]fluoranthene | 14. Naphthalene |
| 7. Benzo[ghi]perylene | 15. Phenanthrene |
| 8. Benzo[k]fluoranthene | 16. Pyrene |

- **Human exposure to PAHs and health effects**

Exposure to polycyclic aromatic hydrocarbons usually occurs by breathing air contaminated by wild fires or coal tar, or by eating foods that have been grilled [64]. Daily human intakes of PAHs are listed in Table 3.17.

- Breathing - most people are exposed to PAHs when they breathe smoke, auto emissions or industrial exhausts; most exhausts contain many different PAH compounds; people with the highest exposures are smokers, people who live or work with smokers, roofers, road builders and people who live near major highways or industrial sources; levels of PAHs in urban air may be 10 times greater than those found in rural areas;
- Drinking and eating - charcoal-broiled foods, especially meats, are a source of some PAH exposure; shellfish living in contaminated water may be another major source of exposure; PAHs may be present in groundwater near disposal sites where construction wastes or ash are buried; people may be exposed by drinking this water; vegetables do not take up significant amounts of PAHs that are in soil;

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- Touching - PAHs can be absorbed through skin; exposure can come from handling contaminated soil or bathing in contaminated water; low levels of these chemicals may be absorbed when a person uses medicated skin cream or shampoo containing PAHs [23].

PAHs may be attached to dust or ash causing lung irritation. Skin contact with PAHs may cause redness, blistering, and peeling. The following health effects can occur after several years of exposure to PAHs:

- Cancer – benzo[a]pyrene, a common PAH, is shown to cause lung and skin cancer in laboratory animals; other PAHs are not known to have this effect; extracts of various types of smoke containing PAHs caused lung tumors in laboratory animals; cigarette smoke will cause lung cancer;
- Reproductive effects - reproductive problems and problems in unborn babies' development have occurred in laboratory animals that were exposed to benzo[a]pyrene;
- Organ system - a person's lungs, liver, skin, and kidneys can be damaged by exposure; in general, chemicals affect the same organ systems in all people who are exposed, however, the seriousness of the effects may vary from person to person; a person's reaction depends on several things, including individual health, heredity, previous exposure to chemicals including medicines, and personal habits such as smoking or drinking; it's also important to consider the length of exposure to the chemical; the amount of chemical exposure; and whether the chemical was inhaled, touched, or eaten [23].

Table 3.17. Daily human Intake of PAHs.

Source	Daily Dose (ng/day)	
	Benzo[a]pyrene	PAHs
Atmosphere	9.5-43.5	200
Water	1.1	30
Food	160-1600	1600-16 000
Cigarette	400	?

The Occupational Safety and Health Administration (OSHA) has set a limit of 0.2 mg/m³ of PAHs. The OSHA Permissible Exposure Limit (PEL) for mineral oil mist that contains PAHs is 5 mg/m³ averaged over an 8-hour exposure period. The National Institute for Occupational Safety and Health (NIOSH) recommends that the average workplace air levels for coal tar products not exceed 0.1 mg/m³ for a 10-hour workday, within a 40-hour workweek. There are

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other limits for workplace exposure for things that contain PAHs, such as coal, coal tar, and mineral oil [64]. Recommended concentration of PAHs, mainly of benzo[a]pyrene, in different media is listed below, in Table 3.18.

Table 3.18. Summary of criteria for polycyclic aromatic hydrocarbons (PAHs) [27].

Water Use	PAHs	Recommended concentration
Drinking Water Supply	B[a]P	0.01 µg/dm ³
Wildlife water supply	None proposed
Livestock water supply	None proposed
Irrigation water supply	None proposed
Fish and/or Shellfish (edible tissue for human consumption) -low consumption of 50 g/week-	B[a]P	4 µg/kg wet weight
Fish and/or Shellfish (edible tissue for human consumption) -moderate consumption of 100 g/week-	B[a]P	2 µg/kg wet weight
Fish and/or Shellfish (edible tissue for human consumption) -heavy consumption of 200 g/week-	B[a]P	1 µg/kg wet weight
Primary contact recreation	None proposed
Food processing industries	B[a]P	0.01 µg/dm ³

Although many different PAHs have been identified, there is limited published toxicological data on them. One of the best characterised and most toxic PAH is benzo[a]pyrene, which is generally used as the indicator PAH.

3.6.4. Banzo[a]pyrene

Benzo[a]pyrene (Fig.3.13) has no specific uses. It is generated by various combustion sources and is also a component or contaminant of such materials as tar and asphalt [32]. Potential sources of B[a]P to our environment are the following [32]:

- Wildfires and prescribed burnings;
- Primary aluminium production;
- Coke ovens;
- Residential wood stoves;
- Burning of scrap tires;
- Open trash burning;
- On-road vehicles;
- Asphalt roofing manufacturing;

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- Industrial boilers;
- Meat charbroilers.

No current commercial production or use of benzo[a]pyrene is known.

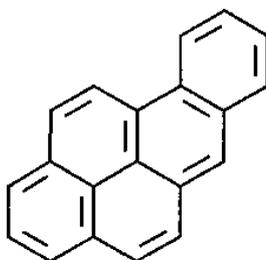


Fig 3.13. Benzo[a]Pyrene formula.

Released benzo[a]pyrene is moderately persistent in the environment. It also readily binds to soils and should not leach to ground water, though it has been detected in some ground water. It has been identified also in surface water, tap water, rain water, waste water, and sewage sludge [71]. If released to water, it B[a]P adsorbs very strongly to sediments and particulate matter. In most waters and in sediments it resists breakdown by microbes or reactive chemicals, but it may evaporate or be degraded by sunlight. Benzo[a]pyrene is lipophilic and is expected to bioconcentrate in aquatic organisms that can not metabolize it, including plankton, oysters and some fish to high levels [32].

Human exposure (Table 3.19) to B[a]P may take place:

- In home by breathing air contaminated by smoke from fireplaces, wood stoves, furnaces burning coal or oil and from food preparation;
- Eating meats and fish that have been smoked or charbroiled;
- Smoking tobacco products;
- Inhaling vehicle exhaust;
- Inhaling fumes from working with coal tar and asphalt, working near charbroiling and high temperature frying equipment, working in coal coking operations and other industrial operations such as asphalt and aluminium production [32].

Table 3.19. Average daily exposition of human population to B[a]P.

Source of B[a]P	Daily dose of B[a]P [µg/day]	Percentage in total daily dose of B[a]P
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Food (generally)	2.10	97%
Air	0.05	2%
Water	0.01	1%
TOTAL	2.16	100%

Experimental data proved that benzo[a]pyrene is carcinogenic to experimental animals. Benzo[a]pyrene is embryotoxic and teratogenic in mice; A reduction in fertility in both male and female offspring was observed in mice following exposure to benzo[a]pyrene in utero. Benzo[a]pyrene undergoes metabolism to reactive electrophiles capable of binding covalently to DNA. It was active in assays for bacterial DNA repair, bacteriophage induction and bacterial mutation. There is sufficient evidence that benzo[a]pyrene is active in short-term tests [32].

No data are available on the systemic (non-carcinogenic) effects of benzo[a]pyrene in humans. Benzo[a]pyrene is readily absorbed following inhalation, oral, and dermal routes of administration. Following inhalation exposure, benzo[a]pyrene is rapidly distributed to several tissues in rats. The metabolism of benzo[a]pyrene is complex and includes the formation of a proposed ultimate carcinogen, benzo[a]pyrene 7,8 diol-9,10-epoxide. Dietary administration of doses as low as 10 mg/kg during gestation caused reduced fertility and reproductive capacity in mice offspring, and treatment by gavage with 120 mg/kg/day during gestation caused stillbirths, resorptions, and malformations [32].

The harmful effects of B[a]P on human are [32]:

- Cancer,
- Skin disorders,
- Harmful developmental and reproductive effects.

Based on United States Environmental Protection Agency (EPA) guidelines, benzo[a]pyrene was assigned to weight-of-evidence group B2, probable human carcinogen [71].

Benzo[a]pyrene is a significant air pollutant in Poland and toxicity coefficient for B[a]P is the highest of commonly determined pollutants. In Poland according to the Cabinet decree form 30 September 1980 maximum acceptable day-average concentration of B[a]P is 50 ng/m³; and for particularly protected areas 30 ng/m³. Permissible concentration of B[a]P in drinking water, according to the Cabinet decree form 4 April 1990, is 15.0 ng/dm³. Permissible daily dose of B[a]P, which can be taken in from different sources, for a 70 kg man is 48 ng.

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World Health Organization (WHO) has established determination standard in drinking water for six polycyclic aromatic hydrocarbons (benzofluoranthene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene), which total concentration should not exceed 200 ng/dm³.

In USA, most federal state standards for B[a]P in the ambient air are in the 0.3-0.7 ng/m³ range as the annual average [25]. The Occupational Safety and Health Administration (OSHA) has established a legally enforceable limit of 200 µg/m³ of all PAHs [26].

A threshold of 5 ng/m³ B[a]P (annual average), the indicator parameter for PAH, is in discussion as an EU-wide directive. In Germany, several federal states adopted a target- B[a]P threshold of 1.3 ng/m³ as the annual average [24].

3.7. Persistent Organic Pollutants (POPs)

The basic components of organic compounds are carbon (C) and hydrogen (H). Organic compounds may also contain such elements like oxygen, nitrogen, sulfur, and chlorine. The examples of organic compounds are: methane (main component of natural gas, non-toxic, flammable), carbon tetrachloride (carcinogenic solvent), benzene (comprises 2-5% of gasoline, flammable, carcinogenic), pesticides, PAHs, PCBs and dioxins. Organic chemicals are characterized by some basic properties, which vary greatly, depending on chemical composition. These are:

- Flammability - ranges from nil to extremely flammable;
- Solubility - amount that will dissolve in water ranges from nil to 100%;
- Density - lighter than water (will float) or heavier than water (will sink);
- Lipophilic character (bioaccumulation and biomagnification).

3.7.1. What are Persistent Organic Pollutants (POPs)?

Persistent organic pollutants (POPs) are carbon containing chemical compounds that, to a varying degree, resist photochemical, biological and chemical degradation. POPs are often halogenated and most often chlorinated [35].

Despite the fact, that many different chemicals may be defined as POPs, 12 POPs, all chlorine-containing organic compounds, have been chosen as priority pollutants by the United Nations Environment Programme (UNEP) for their impact on human health and environment (Table 3.20). The twelve POPs include many of the first generation

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organochlorine insecticides, e.g. DDT, aldrin, industrial chemical products, e.g. PCBs (polychlorinated biphenyls) or, unwanted by-products such as dioxins and furans [34].

Table 3.20. UNEP 12 POPs (also called „Dirty Dozen”).

Pesticides	Industrial Chemical Products	Unwanted By-products
Aldrin Dieldrin Endrin Chlordane DDT Heptachlor Mirex Toxaphene Hexachlorobenzene (HCB)	Polychlorinated biphenyls (PCBs) Hexachlorobenzene (HCB)	Polychlorinated dibenzo-p-dioxins (PCDDs) Polychlorinated dibenzofurans (PCDFs) Polychlorinated biphenyls (PCBs) Hexachlorobenzene (HCB)

3.7.2. Sources of POPs

Although some natural sources of organochlorines are known to exist, most POPs originate almost entirely from anthropogenic sources associated largely with the manufacture, use and disposition of certain organic chemicals. In contrast, HCB, dioxins and furans are formed unintentionally in a wide range of manufacturing and combustion processes [70].

Halogenated, and particularly chlorinated organic compounds have become entrenched in contemporary society, being utilized by the chemical industry in the production of a broad array of products ranging from polyvinyl chloride (millions of tonnes per year) to solvents (several hundreds of thousands of tonnes) to pesticides (tens of thousands of tonnes) and speciality chemicals and pharmaceuticals (thousands of tonnes down to kilogram quantities). In addition, both anthropogenic and non-anthropogenic sources also lead to production of undesirable by-products and emissions often characterized by their persistence and resistance to breakdown (such as chlorinated dioxins). As noted above, organochlorine compounds have a range of physico-chemical properties [34].

3.7.3. Properties of POPs

The carbon-chlorine bond is very stable towards hydrolysis and, the greater the number of chlorine substitutions and/or functional groups, the greater the resistance to biological and photolytic degradation. Chlorine attached to an aromatic ring is more stable to hydrolysis than chlorine in aliphatic structures. As a result, chlorinated POPs are typically ring structures with a chain or branched chain framework. By virtue of their high degree of halogenation, POPs

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have very low water solubility and high lipid solubility leading to their propensity to pass readily through the phospholipid structure of biological membranes and accumulate in fat deposits [70].

One important property of POPs is that of semi-volatility. This property confers a degree of mobility through the atmosphere that is sufficient to allow relatively great amounts to enter the atmosphere and be transported over long distances. This moderate volatility does not result in the substance remaining permanently in the atmosphere where it would present little direct risk to humans and organisms in environment. Thus, these substances may volatilize from hot regions but will condense and tend to remain in colder regions. Substances with this property are usually highly halogenated, have a molecular weight of 200 to 500 and a vapour pressure lower than 1000 Pa [70].

In the environment, organochlorines can be transformed by a variety of microbial, chemical and photochemical processes. The efficiency of these environmental processes are largely dependent on the physico-chemical properties of the specific compound and characteristics of the receiving environment [34].

3.7.4. Environmental Behaviour and Fate of POPs

The behaviour and fate of chemicals in the environment is determined by their chemical and physical properties and by the nature of the environment. The chemical and physical properties are determined by the structure of the molecule and the nature of the atoms present in the molecule. Depending on the structure of the molecule, these physical and chemical properties span a large range of values.

Compounds may be of very low persistence, of low toxicity and be immobile. These compounds are unlikely to present a risk to the environment or to human health. At the other end of the scale are those compounds that are persistent, mobile and toxic and it is this range of the distribution where the toxic and lipophilic POPs are found. Environmental behaviour and exposure are strongly related. Thus, the risk of exposure to a substance will be much lower if the substance is not persistent and the risk, if any, will be localized unless the substance has properties which allow its movement to distant locations [34].

Cyclic, aromatic, cyclodiene-type and cyclobornane type chlorinated hydrocarbon compounds, such as some chlorinated pesticides, with molecular weights greater than 236 g/mol have been noted for their ability to accumulate in biological tissues, and to particularly concentrate in organisms that occupy positions in the upper trophic levels. Not surprisingly,

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these compounds are also known for their persistence in the environment. Compounds included in this class often share many physico-chemical characteristics and include some of the earliest organochlorine pesticides such as DDT, chlordane, lindane, heptachlor, dieldrin, aldrin, toxaphene, mirex and chlordecone. Conversely, the lower molecular weight chlorinated hydrocarbons (less than 236 g/mol) may include a number of alkanes and alkenes (dichloromethane, chloropicrin, chloroform) and are often associated with little acute toxicity, reversible toxicological effects and relatively short environmental and biological half-lives. Bioavailability, that proportion of the total concentration of a chemical that is available for uptake by a particular organism, is controlled by a combination of chemical properties of the compound including the ambient environment and the morphological, biochemical and physiological attributes of the organism itself [70].

Generally, excretion of organic pollutants is facilitated through the metabolic conversion to more polar forms. Because of their resistance to degradation and breakdown, the POPs are not easily excreted and those pollutants (e.g. toxaphene, PCBs etc.) most resistant to metabolism and disposition tend to accumulate in organisms and through the food chain. Notably, some organic pollutants may also be converted to more persistent metabolites than the parent compound, as is the case with the metabolic conversion of DDT to DDE. Similarly, the rapid metabolic conversion of aldrin to its extremely environmentally persistent metabolite dieldrin, is also noteworthy [70].

Most POPs may persist in the environment for periods of several years and may bioconcentrate up to ten thousands fold. These properties of unusual high persistence and semi-volatility, coupled with other characteristics, have resulted in the presence of POPs all over the world, even in regions where they have never been used. POPs have been measured on every continent, at sites representing every major climatic zone and geographic region throughout the world. These include remote regions, where no significant local sources exist and the only reasonable explanation for their presence is long-range transport from other parts of the globe. POPs have been found, on a global scale, in soils, sediments, in the fat of fish and terrestrial animals, as well as in human breast milk. Some of the highest levels have been recorded in the polar areas of both the hemispheres [34].

Through a cycle of long-range transportation, combined with specific physical and chemical characteristics, the wind carries some pesticides and POPs as far as the Arctic. These pesticides, used in more southerly regions, partially evaporate, are carried by winds, then condense under the effect of cold Arctic air and are deposited on the ground. When pollutants

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reach the North they tend to accumulate, and cool temperatures prevent them from evaporating again. POPs can repeat this cycle a number of times and over long distances in a series of "hops," which led to the process being termed the "grasshopper effect" [22].

3.7.5. Influence on Wildlife

POPs are linked by a growing body of evidence to deformities and malfunctions in fish and wild life [34]. Laboratory investigations and environmental impact studies in the wild have implicated POPs in endocrine disruption, reproductive and immune dysfunction, neurobehavioural and disorders and cancer [70].

Studies revealed that a dozen of predators as eagles, cormorants, trouts, minks, turtles and others, suffered significant health impacts including population decline and reproductive dysfunction, eggshell thinning, metabolic changes, deformities and birth defects, cancers, behavioural changes, abnormally functioning thyroids and other hormone system dysfunction, immune suppression, feminisation of males and masculinisation of females [34].

3.7.6. Influence on Human Health

It is possible to document three distinct types of human exposure to POPs.

- High-dose acute exposure - typically results from accidental fires or explosions involving electrical capacitors or other PCB-containing equipment, or high dose food contamination;
- Mid-level chronic exposure - is predominantly due to the occupational exposure, and, in some cases, also due to the proximity of environmental storage sites or high consumption of a POPs-contaminated dietary source, such as fish or other marine animals;
- Chronic, low-dose exposure - is characteristic for the general population world-wide as a consequence of the existing global background levels of POPs with variations due to diet, geography, and level of industrial pollution; low level and population-wide effects are more difficult to study. People are exposed to multiple POPs during their lifetime and most people today carry detectable levels of a number of POPs in their body [35].

The greatest part of human exposure to the 12 POPs is attributed to the ingestion of food. Contamination of food may occur through environmental pollution in the air, water and soil, or through the previous use or unauthorised use of organochlorine pesticides on food crops. Food rich in animal fat, such as meats, fish, and dairy products are the most important means of exposure often due to bioaccumulation through the food chain.

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For some POPs, occupational and accidental high-level exposure, through inhalation and dermal contact, is of concern for both acute and chronic worker exposure. In addition to other exposure routes, worker exposure to POPs during waste management is a significant source of occupational risk in many countries. Short-term exposure to high concentrations of certain POPs has been shown to result in illness and death [35].

A growing body of scientific evidence associates human exposure to individual POPs with cancer, neurotoxic, behavioural, reproductive effects, immutotoxicity and other effects. Evaluation of cancer risk to humans is summarised in Table 3.21. Some POPs are also being considered as a potentially important risk factor in the etiology of human breast cancer by some authors [70]. The mechanism for many of these effects appears to be through disruption of the human endocrine system. Humans appear to be extraordinary sensitive to these chemicals during fetal development (WFPHA, World Federation of Public Health Association, 2000) [34].

More recently some POPs have also been implicated in reduced immunity in infants and children, and the concomitant increase in infection, also with developmental abnormalities, neurobehavioural impairment, as well as cancer and tumour induction or promotion.

Table 3.21. The evaluation of carcinogenic risk to humans for the 12 POPs made by IARC, International Agency for Research on Cancer.

IARC Classification	POPs
Group 1: The agent (mixture) is carcinogenic to humans	2,3,7,8-Tetrachlorodibenzo-para-dioxin (TCDD)
Group 2A: The agent (mixture) is probably carcinogenic to humans	Mixtures of polychlorinated biphenyls
Group 2B: The agent (mixture) is possibly carcinogenic to humans	Chlordane DDT Heptachlor Hexachlorobenzene Mirex Toxaphene (mixtures of Polychlorinated camphenes)
Group 3: The agent (mixture or exposure circumstance) is unclassifiable as to carcinogenicity in humans	Aldrin Dieldrin Endrin Polychlorinated dibenzo-para-dioxins (other than TCDD) Polychlorinated dibenzofurans

3.7.6. Pesticides

The Environmental Protection Agency (EPA) defines a pesticide as "*any substance or mixture of substances intended to prevent, destroy or mitigate any insects, rodents, fungi, or weeds or any other forms of life declared to be pests*" [46].

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Pesticides are employed for many different purposes. Chemicals used in the control of invertebrates include insecticides, molluscicides for the control of snails and slugs, and nematicides for the control of microscopic roundworms. Vertebrates are controlled by rodenticides which kill rodents, avicides used to repel birds, and piscicides used in fish control. Herbicides are used to kill plants. Plant growth regulators, defoliants, and plant desiccants are used for various purposes in the cultivation of plants. Fungicides are used against fungi, bactericides against bacteria, and algicides against algae [3].

Pesticides are released into the environment through human activities. Agricultural area pollution is the greatest and most problematic source of pollution in aquatic environments. Once in the environment, certain pesticides break down relatively quickly, whereas others persist over longer periods of time and can accumulate or transform into contaminant by-products [6]. Half-lives of some exemplar pesticides are listed in Table 3.22. According to their persistency pesticides were divided into three groups:

- Persistent – break down in the range of 75-100% within 2-5 years;
- Moderately persistent – break down within 1-18 months;
- Not persistent – break down within 1-12 weeks.

Table 3.22. Half-life times for pesticides in water and soil.

Pesticides	t1/2 (days)		pH for water and soil
	soil	water	
Lindane	591	>400 ¹	7.4 – 8.0
Dieldrine	365 – 2560	>56 ²	7.4 – 8.0
Chlordane	365 – 1460	53.3 ²	7.4 – 8.0
Heptachlor	304 – 4380	3.5 ²	7.4 – 8.0
Aldrine	194	26.6 ²	7.4 – 8.0
Parathion	30	>4250 ³	5.0 – 6.0
DDT	9 – 3650	>56 ²	7.4 – 8.0
Atrazine	8	3.21 ³	7.0
Malathion	0.8	26.9 ³	9.0

¹ water layer, ² river water, ³ ground water

Degradation of pesticides can take place as a result of bacterial digestion, as well as photochemical and chemical reactions. The process is very often catalysed by metals, soil components and organic compounds. These reactions involve oxidation, reduction, hydrolysis, free radicals interaction and nucleophilic substitution with water. The fact that pesticide undergoes a degradation (which means that it loses its power) does not mean that it becomes an environmentally friendly substance [8], as products of break-down can be even of more toxicity than parent substance.

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Solubility of pesticides depends mainly on their chemical structure. Especially hardly soluble are organochlorine pesticides. Organochlorine pesticides are also very persistent. They resist degradation in normal environmental conditions. They are semi-volatile. At warm temperatures they enter the atmosphere; at cold temperatures they come down to the ground. Finally, they are fat soluble and have a very low water-solubility and they tend to accumulate over a lifetime [47].

Table 3.23. General characteristics of pesticides [8].

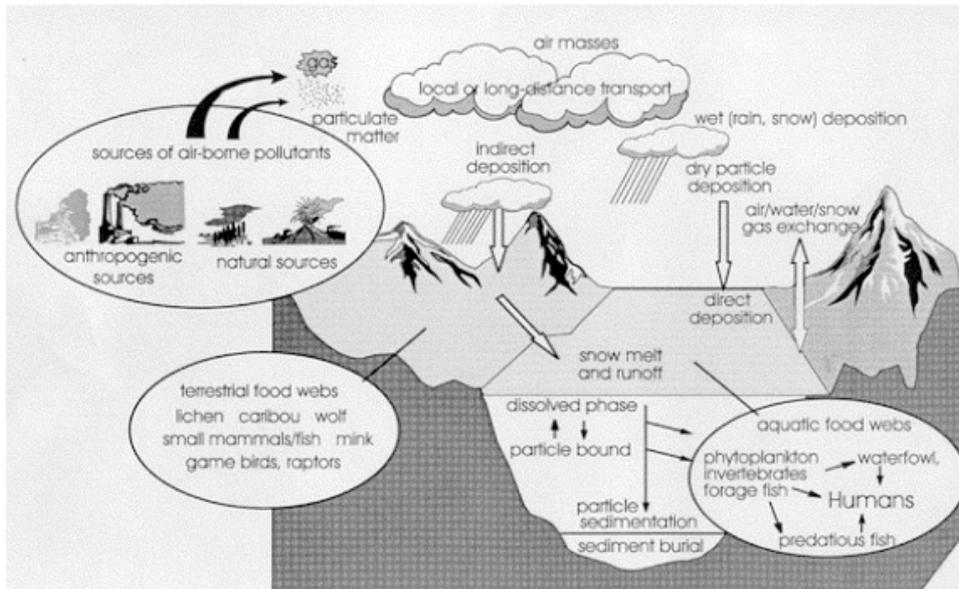
Main classes of pesticides				
Class (examples)	Use	Persistence	Solubility in water	Transport in soil
Chlorinated hydrocarbons (aldrin, dieldrin, DDT, lindane)	insecticides	high	extremely poor	soil erosion
Triazines (atrazine, cyanazine, metribuzin, simazine and amitrole)	herbicides	moderate	good	soil erosion
Phenylureas (monuron)			pH dependent	leaching
Dinitroanilines (benefin)			poor	soil erosion
Phenoxyacetic acid derivatives (2,4-D, 2,4,5-T, mecoprop, MCPB, and MCPA)	herbicides	moderate	good	soil erosion
Phenyl carbamate derivatives (chloroprotham)			good	soil erosion
Ethylenebic-(ditiocarbamate) metal derivatives (maneb)	fungicides	short	moderate	unknown
Pyrethroids	insecticides		extremely poor	soil erosion
Organophosphorus (malathion, parathion azinphos-methyl, diazinon, fenitrothion,)			good	leaching
Carbamates (carbaryl)		good	leaching	

Pesticides can be present in natural waters in dissolved or insoluble form. To a large degree they can be adsorbed on organic and inorganic suspensions [6]. Pesticides adsorbed on soil particles eventually fall onto the bottom of river or lake, staying in sediments [8].

Some pesticides can be mobilized by precipitation and wind. They can be carried by wind in the form of vapour, particles or droplets, which enable them to be transported long distances from their source. Precipitation deposits these contaminants on the ground or in waterways where they may accumulate and/or transform. Figure 3.14 illustrates a typical path taken by certain pesticides in the environment [20].

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Figure 3.14. Pesticide transportation in the environment [21].



Pesticides can get into water few different ways [6]:

- Surface run-off from fields;
- Carried by wind (during and after sprays over forests);
- Industrial sewage (factories producing pesticides);
- Directly introduced into water to fight against aquatic pests, unwanted fish and water insects.

The highest concentration of pesticides is in surface waters and all over the world these concentrations increase. Pesticides percolate into groundwater in a slight amount as they are adsorbed in individual soil layers [6].

Virtually any of the pesticide may be transported into the marine environment if they are sufficiently persistent. However, it is the organochlorines which have received the greatest attention in the context of the marine environment, few of the others having been identified in sea-water or marine organisms [20].

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Prominent amongst the range of pesticides now in common use or widely detected in the environment are chlorophenoxy acids (e.g. 2,4.D), substituted tetrahydrophthalinides (e.g. captan), organochlorines (e.g. DDT, lindane, dieldrin and Mirex), organophosphorus compounds (e.g. malathion) and carbamates (e.g. carbaryl) [20].

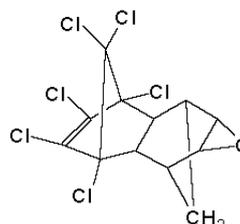
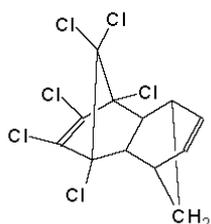
Although insecticide production has remained about level during the last two or three decades, herbicide production has increased greatly as chemicals have increasingly replaced cultivation of land in the control of weeds. Large quantities of pesticides enter water either directly, in applications such as mosquito control, or indirectly, primarily from drainage of agricultural lands). These generally belong to the classes of chlorinated hydrocarbons, organic phosphates, and carbamates [3].

Harmful impact of pesticides on surface waters consists in disturbance of biological balance through toxic effect on biocoenosis (especially fish and zooplankton), disturbance in processes of water self-purification and deterioration of organoleptic parameters [6].

Pesticides are persistent and fat soluble, which makes them being accumulative. Bioaccumulation of pesticides is usually more significant in case of aquatic organisms than terrestrial ones, and can be increased along the food chain [8].

Pesticides can cause harm to humans and animals because they are designed to kill or otherwise adversely affect living organisms. Overseas studies have shown that young children, have an increased risk of getting leukaemia or sarcomas if they live in a home where pesticides are often used, either in the home or garden. Childhood brain cancer has also been linked to the use of some pesticides. Symptoms of short-term exposure to pesticides include: dizziness, vomiting and nausea, headaches, difficulty sleeping, skin rashes, muscle twitches and pain, flu-like fever and breathing difficulties. Exposure to a high concentration of pesticide could result in death. Long term exposure to pesticides can lead to more serious and permanent damage including: cancers, brain damage in children, lowered IQ, permanent kidney damage. Most pesticides persist in the environment for a long time and can continue to have harmful health effects long after they have been applied [48].

a. Aldrin and dieldrin



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Fig. 3.15. Aldrin formula.

Fig.3.16. Dieldrin formula.

Aldrin and dieldrin (Fig. 3.15 and 3.16) are common names for two closely related chemicals that have been widely used for controlling soil insects and certain insect vectors of disease. Aldrin, which readily breaks down to dieldrin in living systems, is used to control soil pests (namely termites) on corn and potato crops. Dieldrin is also an insecticide used on fruit, soil and seed, and has been used to control tsetse flies and other vectors of tropical diseases.

Aldrin and dieldrin readily bind to sediment and are rarely leached to groundwater. Both may be volatilised from sediment and redistributed by air currents, contaminating areas far from their sources. Another route of transfer appears to be surface run off. **Dieldrin now exists everywhere in the environment, but at very low levels.**

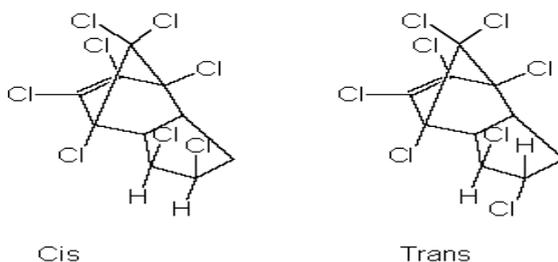
Plants take in these chemicals from the soil and store them. Dieldrin is also stored in animal fat and leaves the body slowly. This persistence, combined with high lipid solubility, provides the necessary conditions for dieldrin to bioconcentrate and biomagnify in organisms. It is likely that dieldrin is bioconcentrated by aquatic organisms rather than bioaccumulated. Dairy products, such as milk and butter, and animal meats were the primary sources of exposure [36].

Aldrin and dieldrin produce adverse enzymatic and hormonal change in fish that lead to impaired reproductive ability. Aldrin bioconcentrates in molluscs and fish, and high levels of dieldrin have been found concentrated in fish, sculpins, snails, and lake trout.

Acute exposure in humans causes adverse effects, between these, are headache, irritability, dizziness, loss of appetite, nausea, muscle twitching, convulsions, loss of consciousness, and possible death. These conditions may persist for a few weeks following exposure, but have not been shown to be permanent [50].

Aldrin and dieldrin have been banned in most developed countries but, aldrin is still used as termiticide in some others.

b. Chlordane



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Fig.3.17. Chlordane formulas.

Chlordane (Fig. 3.17) is a broad spectrum contact insecticide that has been used on agricultural crops. It has also been used extensively in the control of termites. Adheres strongly to soil particles and is not likely to enter groundwater, but can stay in soil for more than 20 years because it is slow to break down. It does not dissolve easily in water but does evaporate into the air. Chlordane builds up in the tissues of fish, birds and mammals.

Chlordane is a known endocrine disruptor. High levels of chlordane can cause damage to the nervous system or liver. People who breathed air containing high concentrations of chlordane or who accidentally swallowed small amounts of it have experienced headaches, irritability, confusion, weakness, vision problems, vomiting, stomach cramps, diarrhea and jaundice [50].

c. DDT

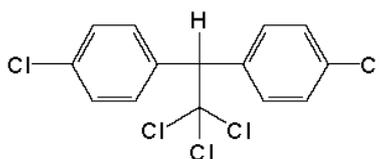


Fig.3.18. DDT formula.

One of the most notorious pesticide used to control pests is a chemical known as DDT (dichlorodiphenyltrichloroethane or 1,1,1-trichloro-2,2-di-(4-chlorophenyl)-ethane) (Fig. 3.18) [3].

DDT is an organochlorine pesticide that was widely used during the Second World War to protect the troops and civilians from the spread of malaria, typhus and other vector borne diseases. After the war, DDT was widely used on a variety of agricultural crops as an insecticide and for the control of disease vectors as well. DDT is one of the earliest and most well known pesticides, and it was widely used until legislative restrictions were imposed after environmental impairments were manifested. Although banned in many countries, DDT is still used in South Africa to control malaria spreading mosquitoes.

DDT is highly insoluble in water and is soluble in most organic solvents. It is semi-volatile and can be expected to partition into the atmosphere as a result. Its presence is ubiquitous in the environment and residues have even been detected in the Arctic. It is lipophilic and partitions readily into the fat of all living organisms and has been demonstrated to

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bioconcentrate and biomagnify. The breakdown products of DDT (1,1-dichloro-2,2-bis(4-chlorophenyl)ethane (DDD or TDE) and 1,1-dichloro-2,2bis(4-chlorophenyl)ethylene (DDE)), are also present virtually everywhere in the environment and are more persistent than the parent compound.

DDT is found in soil, and can be transferred to crops grown on this soil. Root and leafy vegetables contain the highest amounts.

Adverse health effects of DDT in animals include reproductive and developmental failure, possible immune system effects, and the widespread deaths of wild birds after DDT spraying. As is the case with many organochlorine insecticides, a major target of acute DDT exposure is the nervous system. Long term administration of DDT has brought about neurological, hepatic, renal and immunologic effects in animals. Research has shown that DDT prevents androgen from binding to its receptor thereby blocking androgen from guiding normal sexual development in male rats and resulting in abnormalities. Evidence has been found in alligators in which hatchlings from DDE-painted eggs are sexually indeterminate; possessing both male and female reproductive characteristics [36].

DDT primarily affects the nervous system. People more susceptible to the toxic effects of DDT are individuals with diseases of the nervous system, liver or blood. Ingestion or exposure may cause excitability, tremors, seizures, rashes, confusion, convulsions and paresthesia (paralysis) of the tongue and lips. Long-term, low doses have caused changes in levels of liver enzymes, harmful effects on reproduction, and an increased occurrence of liver tumours. DDT is expected to be carcinogenic (Table 3.24). Its continuing presence raises serious concerns regarding potential effects on developing infants [36].

A rise in reproductive abnormalities in both humans and wildlife over the last 20-40 years has caused some scientist to look for environmental factors that may be influencing reproductive capacity. DDT and its metabolites are considered to be environmental oestrogens. In a study in India, a group of men who worked with DDT was found to have decreased fertility and a significant increase in still births, neonatal deaths and congenital defects among their children [37].

Table 3.24. Carcinogeny risk of DDT.

Cancer Classification	Toxic Effects	
	Reproductive	Neurodevelopmental
IARC (1991): Group 2B:	Humans: environmental oestrogen and antiandrogen effects	Humans: single doses from 6 to 10 milligrams:

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<p>possibly carcinogenic to humans.</p>	<p>on foetuses and breast feeding infants.</p> <ul style="list-style-type: none"> • Decreased fertility. • Still births, neonatal deaths and congenital defects among children of chronic exposed workers. (WFPHA, 2000). <p>Birds and mammals: chronic exposure:</p> <ul style="list-style-type: none"> • estrogenic properties and antiandrogenic sexual development feminization of males (alligators and Florida panthers). • Eggshell thinning of offspring. (WFPHA, 2000). 	<ul style="list-style-type: none"> • nausea, headaches, diarrhoea, irritation of the mucous membranes, tremors and convulsions, nervous system abnormalities. (WHO, 1979; WFPHA, 2000). <p>Rats: single or repeated doses (5mg/kg)</p> <ul style="list-style-type: none"> • liver damage, tremors, decreased thyroid function, impaired neurological exposure. (WHO, 1979).
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d. Endrin

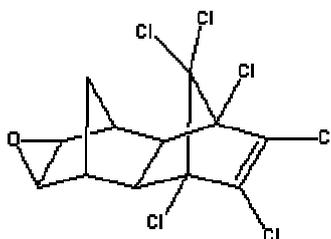


Fig.3.19. Endrin formula.

Endrin (Fig. 3.19) is a rodenticide used to control mice and voles, and an insecticide used on cotton, rice, and maize. Closely related to aldrin and dieldrin, endrin is the most toxic of the three in the aquatic environment and its metabolites are more toxic than endrin itself. In soils endrin is extremely persistent, with a half-life as long as twelve years.

The chemical properties of endrin (low water solubility, high stability in the environment, and semi-volatility) favour its long range transport, and it has been detected in arctic freshwater [36].

Endrin is very toxic to fish, aquatic invertebrates and phytoplankton. Fish kills were observed in areas of agricultural run-off and industrial discharge. Endrin has been found to bioaccumulate in species from algae, pouch snail, flathead minnow, rainbow trout, oyster, and sheepshead minnow [36].

The nervous system is the chief target of acute endrin poisoning. Exposure of humans to a toxic dose may lead within a few hours to such signs and symptoms of intoxication as excitability and convulsions, and death may follow within 2-12 hours after exposure if appropriate treatment is not administered immediately. Endrin might also contribute to improper bone formation, although no human data exist for this effect [36].

e. Heptachlor

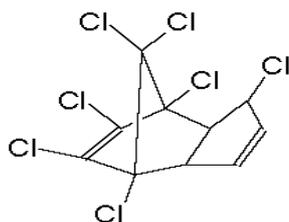


Fig.3.20. Heptachlor formula.

Heptachlor (Fig. 3.20) is insecticide used primarily to kill soil insects and termite, it has also been used to control cotton insects, grasshoppers, and some crop pests, especially for corn. In addition, it has been used to combat malaria [36].

Heptachlor is insoluble in water. It binds to aquatic sediments and bioconcentrates in the fat of living organisms. It evaporates slowly in air.

Heptachlor is metabolised in animals to heptachlor epoxide, whose toxicity is similar to that of heptachlor, and which may also be stored in animal fat. WHO suggests that food is the major source of exposure of heptachlor to the general population, as well as: ingestion of residues in food, inhalation in homes treated for termite control, drinking contaminated water, or skin contact with soil near waste sites or landfills, breast milk from mothers who had high exposures. IARC has classified heptachlor as a possible human carcinogen. It has been banned in more than 50 countries and severely restricted in seven [36].

f. Mirex

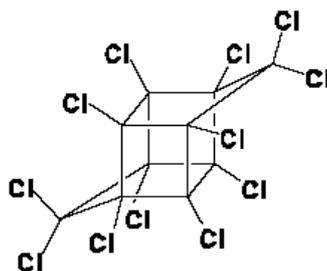


Fig.3.21. Mirex formula.

Mirex (Fig. 3.21) is a bait insecticide used against a number of insect pests. It had been used heavily in South America and South Africa. Secondary use of mirex as a fire retardant in plastics, paints, and electrical goods is currently heavily restricted or banned in most countries.

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Mirex is highly resistant to biodegradation and has a half-life of up to ten years in sediment. In the presence of sunlight, mirex breaks down to a far more potent toxin, photomirex. **Mirex is known to be one of the most stable and persistent pesticides.** Mirex has been detected in Arctic freshwater, terrestrial organisms and in core sediment samples.

The severe effects of mirex on animals, a reduction in germination and emergence of several plant species, has been observed, indicating that mirex is highly toxic to a wide variety of systems. Mirex administered to fish results in kidney lesions and gill damage.

There have been few studies on human exposures, and little data exists for human health effects of mirex. Animal studies have shown several adverse reactions to mirex doses administered through diet. In rats, mirex exhibits toxic effects on fetuses, including cataract formation and it caused liver hypertrophy following long-term, low-dose exposure in rats. Mirex is also associated with suppression of the immune system. Mirex levels in human milk are above average for communities consuming high amounts of fish and sea bird eggs [37].

g. Toxaphene

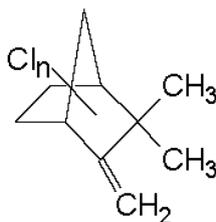


Fig.3.22. Toxaphene formula.

Toxaphene (Fig. 3.22) is an insecticide and acaricide, especially against maggots and on cotton. Toxaphene is not a single compound, but a mixture of over 177 compounds. The production of toxaphene was halted 15 to 20 years ago.

The major route of removal of toxaphene from the soil is through evaporation, but run off from soils treated can be substantial. The half-life of toxaphene in the soil may be as long as twelve years, and it is known to bioconcentrate in organisms.

Toxaphene is toxic for many aquatic organisms and shows sub lethal effects, too. In yearling oysters, for example, it might inhibit shell deposition. Aquatic mammals lack hepatic enzymes that would help metabolise toxaphene congeners. As a result, toxaphene can accumulate in very high levels in their adipose tissues. Concentrations of toxaphene have been found in algae, snail, fathead minnow, brook trout, rainbow trout, oyster, and Atlantic salmon [36].

People are most often exposed to toxaphene through their diet, especially if it includes fish from contaminated source. Acute poisoning from ingestion of prolonged inhalation of

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toxaphene has been reported to cause damage to the lungs, nervous system, liver and kidneys in humans. In at least six cases, ingestion of high doses of toxaphene has been fatal. Inhaled toxaphene had been reported to cause reversible respiratory failure [36].

3.6.2. Hexachlorobenzene

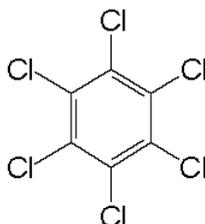


Fig.3.23. Hexachlorobenzene formula.

Hexachlorobenzene (HCB) (Fig. 3.23) is a fungicide that was first introduced in 1945 for seed treatment, especially for control of bunt of wheat. HCB is also a byproduct of the manufacture of industrial chemicals including carbon tetrachloride, perchlorethylene, trichloroethylene and pentachlorbenzene. It is used to make fireworks, ammunition, wood preservatives, dyes and synthetic rubber. Processes that form HCB as by-products are [36]:

- Manufacture of other chemicals;
- Chemical interactions in waste streams of chloralkali;
- Wood-preserving plants;
- Burning of municipal waste.

While intentional production has declined, HCB is also still produced as a by product during the manufacture of several chlorinated chemicals, it has been detected in the flue gas and the fly ash of municipal incinerators and other thermal processes [36]. As a result of past production as well as production processes occurring nowadays HCB is commonly present in the environment. Its distribution in ecosystem is illustrated in Tables 3.25 – 3.27.

Table 3.25. Assumed emission rates kg/h of hexachlorobenzene.

Area	Air	Water	Soil	Sediment	Total
Danmark	0.15	0.02	0	0	0.17
Finland	0.3	0.43	0.17	0.02	0.92
Norway	0.33	0.01	0.05	0	0.39
Sweden	0.47	0.15	0.04	0.002	0.662
Sea areas	0.33	0.27	0	0	0.60
Total Nordic countr .	1.8	0.3	0.06	0.04	2.20
Bay of Bothnia	0.04	0.012	0	0	0.052

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Baltic Proper	0.27	0.15	0	0	0.42
Skagerrak/North Sea	0.17	0.04	0	0.001	0.211
Barents Sea	1.19	0.21	0	0	2.4

Table 3.26. Concentrations g/m³ of hexachlorobenzene.

Area	Air	Water	Soil	Sediment	Fish
Danmark	3.5 • 10 ⁻¹⁰	7.7 • 10 ⁻⁷	1.8 • 10 ⁻⁵	1.4 • 10 ⁻³	0.0010
Finland	1.0 • 10 ⁻¹⁰	3.1 • 10 ⁻⁷	2.5 • 10 ⁻⁴	8.2 • 10 ⁻⁴	0.0037
Norway	1.0 • 10 ⁻¹⁰	5.3 • 10 ⁻⁸	7.4 • 10 ⁻⁵	1.3 • 10 ⁻¹⁰	0.00064
Sweden	1.0 • 10 ⁻¹⁰	9.7 • 10 ⁻⁸	4.9 • 10 ⁻⁵	2.1 • 10 ⁻⁴	0.00122
Sea areas	1.0 • 10 ⁻¹⁰	1.7 • 10 ⁻⁷	5.74 • 10 ⁻⁶	1.1 • 10 ⁻³	0.00187
Total Nordic countr.	1.0 • 10 ⁻¹⁰	2.5 • 10 ⁻⁸	3.1 • 10 ⁻⁵	1.8 • 10 ⁻⁴	0.00028
Bay of Bothnia	8.4 • 10 ⁻¹¹	1.9 • 10 ⁻⁸	6.2 • 10 ⁻⁶	5.5 • 10 ⁻⁵	0.00025
Baltic Proper	1.0 • 10 ⁻¹⁰	2.3 • 10 ⁻⁸	5.5 • 10 ⁻⁶	1.5 • 10 ⁻⁴	0.00026
Skagerrak/North Sea	3.0 • 10 ⁻¹⁰	4.1 • 10 ⁻⁸	1.5 • 10 ⁻⁵	2.7 • 10 ⁻⁴	0.00046
Barents Sea	7.0 • 10 ⁻¹¹	6.3 • 10 ⁻⁹	6.9 • 10 ⁻⁶	2.8 • 10 ⁻⁶	9.7 • 10 ⁻⁵

Table 3.27. Mass distribution per cents of hexachlorobenzene.

Area	Air	Water	Soil	Sediment
Danmark	4.10	2.57	36.95	56.39
Finland	0.167	0.949	67.26	31.62
Norway	0.727	0.119	95.51	3.64
Sweden	0.818	1.29	62.72	35.16
Sea areas	0.912	2.97	7.91	96.11
Total Nordic countr.	1.16	1.49	42.55	1.82
Bay of Bothnia	1.41	6.27	0.051	92.27
Baltic Proper	0.680	2.98	0.0031	96.34
Skagerrak/North Sea	1.06	2.91	0.021	96.02
Barents Sea	4.34	78.20	6.40	17.44

Organisms generally accumulate HCB from water and from food, although benthic organisms may also accumulate HCB directly from sediment. The bioavailability of sediment-bound HCB is inversely correlated to sediment organic carbon content, and varies with the feeding habits of the organisms. Field studies indicate that exposure via food is important for organisms at higher trophic levels, as significant biomagnification has been observed in several studies in natural aquatic ecosystems. Long-range atmospheric transport of HCB to the Arctic and other remote areas is a well-recognized phenomenon. The substance has been detected in Arctic air, snow, seawater, vegetation and biota.

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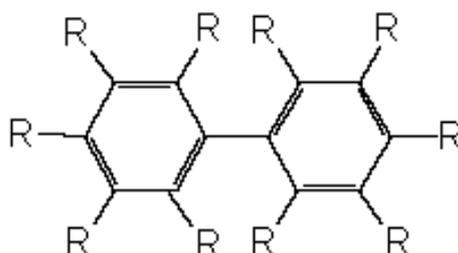
HCB is toxic to humans and animals when long-term exposure occurs. It can occur as a result of consumption of dairy products or meat from cattle grazing on contaminated pastures, eating low levels in contaminated food, eating or touching contaminated soil, or drinking small amounts in contaminated water, breathing low levels in contaminated air, working in a factory that uses or produces HCB unintentionally. In case of babies exposure takes place when drinking contaminated breast milk from exposed mothers [36].

Acute high dose exposure to HCB is associated with porphyria cutanea tarda due to its liver toxicity. HCB is also associated with enlarged thyroid glands, scarring, and arthritis exhibited in offspring of accidentally exposed women, and cancer (Table 3.28). Children born to mothers known to have ingested HCB-tainted food during pregnancy experienced acute illnesses and rashes. These children were additionally exposed through breast milk. Follow up studies reported porphyria cutanea tarda, reduced growth, and arthritic symptoms in children directly exposed to contaminated bread or mothers' milk [40].

Table 3.28. Hexachlorobenzene health effects.

Cancer Classification	Toxic Effects	
	Neurodevelopmental	Others
IARC (1987): Group 2B: possibly carcinogenic to humans.	Humans: high dose, acute exposure: <ul style="list-style-type: none"> • porphyria cutanea tarda with follow-up of several years in some cases. • Enlarged thyroid gland, scarring, arthritis in children of exposed mothers and exposed to breast milk. Animals: acute neurologic toxicity with symptoms such as tremors, paralysis, incoordination, weakness, and convulsions. (WFPHA, 2000)	Rats: low dose: <ul style="list-style-type: none"> • low dose: alteration of steroid production of adrenal cortex cells. • Damage to the liver and spleen. Maternal (chronic) exposure led to teratogenic effects including cleft palate, changes in rib development, kidney malformation. New born death related to cumulative exposure through milk. (WFPHA, 2000)

3.6.3. Polychlorinated Biphenyls (PCBs)



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Fig.3.24. General formula for PCBs.

Polychlorinated biphenyls (PCBs) (Fig. 3.24) are a family of 209 chemical compounds formed by the addition of chlorine (Cl_2) to biphenyl ($\text{C}_{12}\text{H}_{10}$), which is a dual-ring structure comprising two 6-carbon benzene rings linked by a single carbon-carbon bond. The nature of an aromatic ring allows a single attachment to each carbon. This means that there are 10 possible positions for chlorine substitution, all of them listed in Table 3.29. Species with a single chlorine substituent are called monochlorobiphenyl (or just chlorobiphenyl). Species with two chlorines are called dichlorobiphenyl, and those with three through ten chlorines, in order, are called: tri-, tetra-, penta-, hexa-, hepta-, octa-, nona- and deca-chlorobiphenyl [30]. PCB is complex in many ways, not the least of which is the nomenclature used to name and otherwise identify its various species. Any single, unique, well-defined chemical compound in the PCB category is called a *congener*. The name of a congener specifies the total number of chlorine substituents and the position of each chlorine [30]. For example 4,4'-dichlorobiphenyl is a congener comprising the biphenyl structure with two chlorine substituents, one on each of the two carbons at the "4" (also called "para") positions of the two rings [54]. *Homologs* are subcategories of PCB congeners having equal numbers of chlorine substituents. For example, the tetrachlorobiphenyls are all PCB congeners with exactly 4 chlorine substituents that may be in any arrangement. The numbers of congeners in each homolog are given in the following Table 3.29. [30].

Table 3.29. PCB homologs.

Homolog	Molecular formula	Cl Substituents	PCB Congeners
Monochlorobiphenyl	$\text{C}_{12}\text{H}_9\text{Cl}$	1	3
Dichlorobiphenyl	$\text{C}_{12}\text{H}_8\text{Cl}_2$	2	12
Trichlorobiphenyl	$\text{C}_{12}\text{H}_7\text{Cl}_3$	3	24
Tetrachlorobiphenyl	$\text{C}_{12}\text{H}_6\text{Cl}_4$	4	42
Pentachlorobiphenyl	$\text{C}_{12}\text{H}_5\text{Cl}_5$	5	46
Hexachlorobiphenyl	$\text{C}_{12}\text{H}_4\text{Cl}_6$	6	42
Heptachlorobiphenyl	$\text{C}_{12}\text{H}_3\text{Cl}_7$	7	24
Octachlorobiphenyl	$\text{C}_{12}\text{H}_2\text{Cl}_8$	8	12
Nonachlorobiphenyl	$\text{C}_{12}\text{HCl}_9$	9	3
Decachlorobiphenyl	$\text{C}_{12}\text{Cl}_{10}$	10	1

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With few exceptions, PCB was manufactured as a complex mixture of congeners, through progressive chlorination of batches of biphenyl until a certain target percentage of chlorine by weight was achieved. Commercial mixtures with higher percentages of chlorine contained higher proportions of the more heavily chlorinated congeners, but all congeners could be expected to be present at some level in all mixtures [30].

• **Properties and Use of PCBs**

PCBs were first synthesized industrially in the USA in 1929. They were manufactured by treating biphenyl with chlorine, which produces a mixture of individual PCB compounds whose composition depends on the proportion of chlorine to biphenyl [4]. At the beginning they were used as paint components, especially printing ones, and next as plasticizers and isolating materials in transformers [1].

PCB compounds have a variety of industrial uses according to their chemical properties. Those polycyclic compounds, which have high chlorine content, are chemically and thermally stable. They also have good hydraulic and electrical properties and are fire resistant. The less chlorinated benzenes and substituted benzenes are generally more reactive and find uses primarily as chemical intermediates [20]. In consistency, PCBs range from light oily fluids to greasy or waxy substances and are clear to yellow in colour [55].

Table 3.30. Chlorinated biphenyls - composition and properties of isomer group [20].

Number of chlorine atoms	Number of isomers	M.W.	%C1	Solubility in water (pg/dm ³)
0	1	154	0	
1	3	189	19	1100-5900
2	12	223	32	80-1400
3	24	257	41	78-85
4	42	291	49	34-180
5	46	326	54	22-31
6	42	361	59	88
7	24	395	63	
8	12	430	66	7
9	3	464	69	
10	1	499	71	15

The flame resistance of the polychlorinated biphenyls made them ideal for use in electrical products because they did not burn, break down, or react with other chemicals. Originally produced for use as flame retardants and as electrical insulators in transformers, capacitors, and other electrical equipment. PCBs were used in heating coils, carbonless carbon paper,

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lubricating oils for industrial drills, caulking compounds for skyscraper windows, electrical motors in refrigerators, in air conditioners, typewriters, power saws, and the like. At one time or another, a wide variety of products including cereal boxes, degreasers, varnishes, lacquers, waterproofing materials, and bread wrappers used PCBs. The unique properties of PCBs allowed them to be used in the manufacturing of many common products such as plastics, adhesives, paints, and varnishes [55].

During the period 1929-1970 world production of PCBs increased steadily and the compounds were used worldwide in a variety of applications (Table 3.31). When it became recognized that PCBs in the environment were proving a significant risk, production was drastically cut back and has now essentially ceased. The total cumulative world production of PCBs has been estimated at 750 000 tonnes, of which some 300 000 tonnes (40%) has been dispersed into the environment. The remainder (60% - 450 000 tonnes) is either still in use or is present in landfills or other waste disposal sites. PCB fluids are present in many older transformers, fluorescent lighting fixtures, and other electrical devices and appliances. These are vulnerable to release into the environment, as older components can leach and may represent a significant hazard to both terrestrial and aquatic systems [38].

Table 3.31. Production and uses of halogenated aromatic compounds (more than one ring).

Compound	Major trade names	World production (1000 t a-l)	Major uses
Polychlorinated biphenyls (PCB)	Aroclor Phemoclор Kanechlor Clophen Fenclor Santotherm	70a	Capacitor dielectric, transformer coolant, hydraulic fluid, plasticizer, heat transfer fluid
Polychlorinated triphenyls (PCT)	Aroclor Kanechlor	5?	Adhesives and sealants
Polychlorinated naphthalenes (PCN)	Halowax	5?	Capacitor dielectric, oil additive
Polybrominated biphenyls (PBB)	Firemaster	5b	Fire retardant

^a Peak annual rate for 1969-1970.

^b Peak annual rate for 1974.

- **Environmental Fate of PCBs**

PCBs entered the air, water, and soil during their manufacture, use, and disposal; from accidental spills and leaks during their transport and from leaks. PCBs were released into the

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atmosphere through sewers, smokestacks, weathering of asphalt and other substances containing PCBs, and burning PCB- containing products. PCBs can still be released to the environment from hazardous waste sites, illegal or improper disposal of industrial wastes and consumer products, leaks from old electrical transformers containing PCBs and burning of some wastes in incinerators [56]. Table 3.32 presents the main sources of environmental PCBs, and Table 3.33 illustrates the distribution of PCBs in the environment [4].

Table 3.32. Main sources of environmental PCBs [4].

Source	Annual input percentage	Type of PCS (% chlorine)
Evaporation from plasticizers	4.5	48-60
Evaporation during mineralization	1	42
Leakages and disposal of industrial waste	13	42-60
Incineration	9	mainly 42
Disposal at dumping grounds	52.5	42-60
Net increase in current usage	20	42-54

The very characteristic of the PCBs that made them wonderful for use in manufacturing makes them problematic in the environment. PCBs are very persistent: they are generally unalterable by microorganisms or by chemical reaction [55].

Table 3.33. Distribution of PCBs in the environment (t) [4].

	Continents and coastal zone	Ocean	Total
Atmosphere	500	790	1,290
Lakes and rivers	3,500	-	3,500
Sea water	2,400	230,000	232,400
Soil	2,400	-	2,400
Bottom sediments	130,000	110	130,110
Biota	4,300	270	4,570
TOTAL	143,000	231,000	374,000
Global PCBs usage			783,000
Amount of PCBs formed in degradation and combustion processes			43,000
Global production			1,200,000

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In water, PCBs are adsorbed on sediments and other organic matter. Experimental and monitoring data have shown that PCBs concentration in sediment and suspended matter are higher than those in associated water columns. On the basis of their water solubilities and n-octanol-water partition coefficients, the lower the chlorinated PCB congeners will sorb less strongly than the higher chlorinated isomers. Although adsorption can immobilise PCBs for relatively long periods in the aquatic environment, desorption into the water column has been shown to occur by both abiotic and biotic routes. The substantial quantities of PCBs in aquatic sediments can therefore act as both an environmental sink and a reservoir of PCBs for organisms. Most of the environmental load of PCBs has been estimated to be in aquatic sediment. Even though many countries have controlled both use and release of PCBs and new input into the environment is on a reduced scale compared with the past, the available evidence suggests that the cycling of PCBs is causing a gradual redistribution of some congeners towards the marine environment [38].

Over the decades large quantities of PCBs have been disposed of in landfill tips; unfortunately PCBs do not necessarily remain at the sites where they have been dumped. Degradation on land and at sea occurs very slowly, and their partial volatility at ambient temperatures provides a mechanism whereby PCBs can become remobilized and released into air from soil and water. Because of these transport processes they are now present in trace amounts (ppb) in all surface soils and sediments, and are also associated with surface deposits on vegetation, Data presented in Table 3.34 confirm the thesis that PCBs are present in all kinds of samples [4].

Table 3.34. Typical concentrations of PCBs in the environment compartments [4].

Compartment	Typical concentration
Air (rural)	0.05 mg/m ³
(urban)	1 - 5 ng/m ³
Surface soil	2 - 50 µg/kg
Vegetation	10 µg/kg
Water	2 ng/dm ³
Man (adipose tissue)	1 mg/kg
(breast milk)	10 µg/dm ³
Marine mammals (blubber)	5-50 mg/kg (wet weight)
Otter (fat)	5 - 200 mg/kg (wet weight)

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The widespread use of chloropesticides and PCBs has led to a ubiquitous occurrence of these compounds in the environment. Even after a ban on the use of some chloropesticides and of PCBs in open systems, the global deposition of PCBs in Germany is around 100 mg/ha per year due to global dispersion. Sediment core collected in the southern part of the Baltic Proper was analyzed for DOT compounds, PCBs including the coplanar congeners, polybrominated diphenyl ethers (PBDE) and polychlorinated naphthalenes (PCN). The results of the sediment analyses indicate the presence of PCBs, DDT and PBDE compounds in sediment layers dating from the 1950's and later. Neither coplanar PCB nor PCN were detected at any level of the sediment core. The PCB concentrations indicate a slight increase in levels during the last decades, while there were no changes in the level of DDT compounds [4].

- **Effects on The Aquatic Environment**

During the mid-1960s, some environmental scientists began seeing an increase of PCBs in animal tissues. In 1978, the U.S. Environmental Protection Agency banned the use of PCBs in all but closed systems of manufacturing. In 1979, the use of PCBs was banned in all applications [55].

The stable nature of PCBs leads to accumulation in the fatty tissues of animals once the PCBs are released into the environment. These accumulations increase as the tissue from contaminated animals moves through the food web. Because of bioaccumulation, the concentration of PCBs found in fish tissues is expected to be considerably higher than the average concentration of PCBs in the water from which the fish were taken [55].

PCBs transfer more efficiently through aquatic than terrestrial food chains. Consequently, the highest reported concentrations of PCBs in the environment occur consistently in fish-eating higher predators: marine mammals, otters and fish-eating birds [4].

Several factors determine the degree of bioaccumulation in adipose tissues: the duration and level of exposure, the chemical structure of the compound, and the position and pattern of substitution. In general, the higher chlorinated congeners are accumulated more readily. Experimentally determined bioconcentration factors of various PCBs in aquatic species (fish, shrimp, oyster) range from 200 up to 70 000 or more. In the open ocean, there is bioaccumulation of PCBs in higher trophic levels with an increased proportion of higher chlorinated biphenyls in higher ranking predators [38].

- **Effects on humans**

PCBs are extremely toxic. Individuals can be exposed to PCBs through a variety of means. PCBs can affect humans through:

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- Inhalation (respiration);
- Digestion;
- Through the skin (dermal absorption).

Old appliances such as TVs and refrigerators may leak small amounts of PCBs when hot, as can old fluorescent lighting fixtures. Eating food containing PCBs is a means of exposure. Breathing air near contaminated sites and drinking PCB contaminated well water are two additional means of exposure. PCBs can be passed to a child through its mother's milk. People who work with equipment containing PCBs are potentially exposed [55].

Because of their high persistence, and their other physical and chemical properties, PCBs are present in the environment all over the world. In past years, many thousands of samples of different foodstuffs have been analysed in several countries for contaminants including PCBs.

The levels for the most important PCB-containing food items were:

- Animal fat 20 - 240 µg/kg of fat;
- Cow's milk 5 - 200 µg/kg;
- Butter 30 - 80 µg/kg;
- Fish 10 - 500 µg/kg, on a fat basis.

The major foods in which contamination with PCBs needs consideration are fish, shellfish, meat, milk, and other dairy products. Median levels in fish, reported in various countries, are of the order of 100 µg/kg (on a fat basis). PCBs are affecting more heavily population of cold areas of the planet. A study in the late 1980s showed that PCB levels in milk of Inuit women from the east coast of Hudson Bay in northern Quebec were approximately five times higher than in women of southern Canada [38].

In acute exposure, vapour can irritate the eyes, nose, and throat and cause an acne-like rash called chloracne. High exposure can damage the liver and may damage the nervous system causing numbness, weakness, and tingling in arms and legs. Human fatal exposures of PCBs are associated with neural and developmental changes, lower psychomotor scores, short-term memory and spatial learning effects, and long-term effects on intellectual function. Chronic exposure may result in reproductive system problems. PCBs can sometimes affect the immune system [55].

Few studies of workers indicate that PCBs were associated with certain kinds of cancer in humans, such as cancer of the liver and biliary tract. The EPA and the International Agency

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for Research on Cancer (IARC) have determined that PCBs are probably carcinogenic to humans (Table 3.35) [56].

Neurological dysfunction had been associated with perinatal PCB exposure in several Dutch studies. Perinatal exposure to PCBs may impair immune responses to infection as suggested by a 20-fold higher incidence of infectious diseases and ear infections in a study of Inuit infants with high PCB exposure compared to individuals in a lesser exposed population [38].

Table 3.35. Toxic effects of PCBs exposure.

Cancer Classification	Toxic Effects		
	Neurodevelopmental	Reproductive	Immune System
IARC (1987): Group 2A: probably carcinogenic to humans.	Human fetal exposure: neural and developmental changes, lower psychomotor scores, short-term memory and spatial learning effects, long term effects on intellectual function. Neurological dysfunction. (WFPHA, 2000). Rats, mice, monkeys and quail low doses for twelve months: <ul style="list-style-type: none"> • neural changes. • Impaired or abnormal neuromotor function, (Rhesus monkeys). (WFPHA, 2000). 	Seals and porpoises: <ul style="list-style-type: none"> • induced reproductive impairment. Minks: <ul style="list-style-type: none"> • embryo toxicity. Birds: <ul style="list-style-type: none"> • eggshell thinning. (WFPHA, 2000). Turtles (read eared slider): <ul style="list-style-type: none"> • hormone disrupting effects with sex determination (population of only females). (WFPHA, 2000). 	Humans: perinatal exposure may impair immune responses to infection. (WFPHA, 2000).

• **What can be done about PCBs?**

There are ways of destroying PCBs in both water and soil, effectively removing them from the environment.

PCBs can be destroyed by burning. Therefore, many items containing PCBs can be destroyed appropriately and safely in hazardous waste incinerators that use burners at appropriate levels of heat. Conditions for PCBs combustion requires heat in range of 1000 - 1200°C and 3% oxygen excess within 1.5 -2.0 s. In USA combustion effectiveness required by EPA is equal to 99.9999%. It is almost impossible to achieve such level of measurement accuracy (0.0001%) in case of a process so difficult for analysis proceeding. Additional errors which can occur are connected with flow velocity, sampler location and amount of products adsorbed on out-flowing dusts [1].

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Two different technologies are being used for on-site destruction of PCBs. The first is the use of plasma arc torches. This is used for many soils that are contaminated with large amounts of PCBs. The second process is a bacterial process or bioremediation that is used for rivers where large sediment concentrations of PCBs are found. Presently there are more than 20 strains of bacteria capable of using biphenyl as their sole source of carbon [55].

Destruction techniques for wastes containing PCB compounds with the use of incinerator ships are of particular relevance to the marine environment. The most well known of these ships is the *M/T Vulcanus* which is now operated by the company Chemical Waste Management Inc. and which has been operated since about 1972 in the North Sea, American waters and the South Pacific.

The ship can carry about 3500 m³ of liquid waste which is burned at a rate of approximately 15 m³/h. Combustion temperatures are in excess of 1300°C and tests at American incineration sites in the Gulf of Mexico and the South Pacific have indicated that destruction efficiencies are greater than 99.99% of PCBs and chlorobenzenes and greater than 99.9% for TCDFs and Herbicide Orange.

The claimed advantage of incinerating chlorinated wastes at sea is that the hydrochloric acid produced is rapidly neutralized by the surrounding sea-water. There are therefore considerable cost savings because there is no need to scrub the exhaust gases before discharge as there is in the equivalent land-based operation [20].

- **Regulations**

The EPA has set a limit of 0.0005 mg/dm³ of PCBs in drinking water. Discharges, spills or accidental releases of 1 pound or more of PCBs into the environment must be reported to the EPA.

The Food and Drug Administration (FDA) requires that infant foods, eggs, milk and other dairy products, fish and shellfish, poultry and red meat contain no more than 0.2-3 ppm of PCBs (0.2-3) in food. Many states have established fish and wildlife consumption advisories for PCBs [56].

Low levels of PCBs have been shown to cause health problems in humans. Two parts per million (ppm) of PCBs is the highest acceptable concentration level in fish. The airborne limit of permissible exposure is 1 mg/m³ (42% Chlorine) and 0.5 mg/m³ (54% Chlorine) over eight hours of exposure.

The U.S. Food and Drug Administration requires that dairy, poultry, seafood and infant products not contain PCBs in more than 0.2-3 ppm [38].

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- For the protection of freshwater and marine aquatic life and consumers of fish and shellfish (e.g., wildlife), it is recommended that the total PCB concentration in water should not exceed 0.1 ng/dm^3 . Additionally it is recommended that the concentrations of:
 - a. 3,3',4,4'-tetrachlorobiphenyl (PCB #77) should not exceed 0.04 ng/dm^3 ;
 - b. 2,3,3',4,4'-pentachlorobiphenyl (PCB #105) should not exceed 0.09 ng/dm^3 ;
 - c. 3,3',4,4',5,5'-hexachlorobiphenyl (PCB #169) should not exceed 0.06 ng/dm^3 ;
 - d. 3,3',4,4',5-pentachlorobiphenyl (PCB #126) should not exceed 0.00025 ng/dm^3 .
- To protect wildlife dependent on aquatic life for food, it is recommended that the total concentration of PCBs in whole fish and/or shellfish should not exceed $0.1 \text{ } \mu\text{g/g}$ wet weight.
- To protect human consumers from PCB residue in aquatic life, it is recommended that the concentration of PCBs in the edible portion of fish and/or shellfish should not exceed $2.0 \text{ } \mu\text{g/g}$ wet weight.
- To protect aquatic life and consumers of aquatic life (e.g., wildlife), it is recommended that the concentration of PCBs in freshwater and marine sediments containing 1.0% organic carbon should not exceed $0.02 \text{ } \mu\text{g/g}$ -sediment (or $2 \text{ } \mu\text{g/g}$ -organic carbon, when expressed on an organic carbon basis).
- Criteria for PCBs in water for wildlife use are not recommended, since a safe level would be much higher than that expected to occur in surface waters. It is recommended that the total concentration of PCBs in irrigation water should not exceed $0.5 \text{ } \mu\text{g/dm}^3$.

PCBs were a valuable family of chemicals for manufacturing throughout much of this century. Looking back, it is possible to identify problems caused by PCBs and consider what might have been done differently. The reality is that society benefited from the use of these chemicals, and we now must deal with the negative legacy of these chemicals in the environment [55].

3.7.7. Dioxins and Furans

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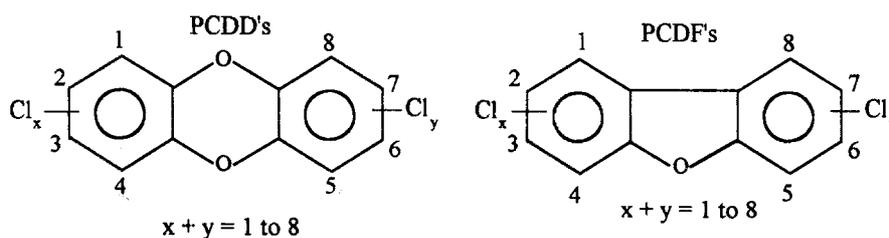


Fig. 3.25. General formulas of dioxin and furan [4].

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) (Fig. 3.25) are two structurally similar families of compounds that include 75 and 135 congeners, respectively.

PCDDs and PCDFs do not occur naturally and are not manufactured, but are by-products produced in ppm range when some wood preservatives and herbicides are manufactured. PCDDs and PCDFs are present as impurities in chlorophenols and polychlorinated biphenyls. In addition of most relevance, they are found in combustion products, the ash, stock effluents, water and other process fluids from the combustion of municipal wastes, coal, wood and industrial waste. It is also known that PCDDs and PCDFs are produced at very low levels from certain motor vehicle exhausts using leaded gasoline, the scavenger dichloroethane acting as the precursor for PCDDs and PCDFs. PCDDs and PCDFs have also been detected in used lubricating oil derived from chlorinated additives in the air or gasoline [4]. The sources of dioxins are listed below, in Table 3.36.

- **Environmental fate and effects on wildlife**

Because dioxin is very chemically stable, and does not break down easily in the environment, they are often found in high concentrations in sediments, sludge and dusts. Because most dioxin accumulates in the fatty tissues of animals they are particularly evident in aquatic, bottom dwelling organisms that are continually in contact with sediments, and in filter feeders that ingest particulate matters suspended in water. Once released into the environment, dioxin can be transported vast distances along air and ocean currents [41].

As it travels throughout the global environment dioxin bioaccumulates and can take decades to break down [41]. There is substantial evidence to indicate that populations of wildlife species high on the food chain are suffering health damage due to reproductive and developmental impairment due to background exposures to dioxins and related compounds [39].

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Table 3.36. Dioxin source categories identified and/or described by USEPA [41].

Combustion sources		
Municipal waste incinerators	Biogas combustion	Carbon reactivation
Open burning of domestic waste	Pulp & paper mill – kraft black liquor recovery boilers	Forest & brush fires
Medical waste incinerators	Combustion of landfill gas	Waste tire combustion
Hazardous waste incinerators Dedicated (commercial & on-site) Industrial boilers/furnaces	Cement Kilns Conventional fuels Hazardous waste	Accidental fires Structural fires Vehicle fires PCB fires Landfill fires
Petroleum refining catalyst regeneration	Pulp & paper mill sludge incineration	Cigarette smoking
Light – weight aggregate kilns	Lime kilns	Crematoria
Sewage sludge incinerators	Asphalt mixing plants	Candles
Kraft Mill Wood Residue Boilers		
Chemical manufacturing		
Chlorine & chlorine dioxide Bleaching pulp & paper mills	Mono-to tetrachlorophenols	Chloranil
Elemental chlorine	Pentachloro phenol	Printing Inks
Sodium hypochlorite	Chlorobenzenes	Tetrachlorobisphenol-A
Metal chlorides Iron chlorides Aluminium chlorides Copper chlorides	Ethylene dichloride/vinyl Chloride monomer (EDC/VCM)	Alkylamine tetrachlorophenate
PCB's (leak and spills)	Polyvinyl chloride (PVC)	Chlorinated pesticides
Dioxazine dyes & pigments		2,4 – D
Phthalocyanine dyes & pigments		
Power/energy generation		
Oil combustion Industrial/Utility Residential/Commercial	Motor vehicle fuel combustion Leaded gasoline Unleaded gasoline Diesel fuel	Wood combustion Industrial; & residential Waste wood salt-soaked preservative-treated PVC-clad
Coal combustion Electric utilities/industrial Residential/commercial		
Metal smelting & refining & processing		
Primary nonferrous metals	Secondary nonferrous metals	Iron & steel production
Magnesium	Aluminium	Ore sintering
Nickel	Copper	Coke production
Aluminium	Lead	Electric arc furnaces
Copper	Scrap electric wire recovery	Ferrous foundries
Drum & barrel reclamation furnaces		
Biological & photochemical processes		
Biotransformation of chlorophenols and highly chlorinated dioxins & furans		
Phototransformation of chlorophenols		
Photolysis of highly chlorinated dioxins & furans		
Reservoir sources		
Sediments	Forests	Landfills
Soils	Pentachlorophenol-treated wood	

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In water environment exposure to dioxin-like compounds have been linked to large -scale hormonal, reproductive and developmental impairment among numerous species of predator birds fish and wildlife; these impacts are primarily transgenerational, affecting the offspring of the exposed organisms [39].

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are two classes of environmental contaminants which are now present in all parts of the environment (atmosphere, water and soil). The concern over dioxins and furans arises since they are highly toxic to man at ultra trace levels (ppt), they are environmentally stable and present difficult analytical problems because of interferences and low concentrations. PCDDs and PCDFs with the 2,3,7,8-configuration (17 congeners) are the most toxic for experimental animals.

The overall toxicity of a dioxin containing mixture is assumed to be the Toxic Equivalent (TEQ) of a stated amount of pure 2, 3, 7, 8-tetrachloro-dibenzo-p-dioxin (TCDD) (Fig.3.26), the most potent, hazardous and well-studied dioxin [39].

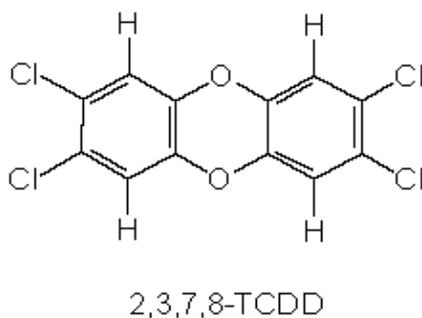


Fig.3.26. 2, 3, 7, 8-tetrachloro-dibenzo-p-dioxin formula.

- **Effects on humans**

Food is a major source of dioxins and furans in the general population, with food of animal origin contributing the most to human body burdens [36]. Approximately 90% of human exposure to dioxin comes from food, especially from beef, fish, and dairy products. Contamination in the food supply comes from dioxin particles that are deposited in water or soil and then proceed up the food chain through fish and livestock, ultimately reaching human tissues through the food we eat. Dioxin bioaccumulates, becoming increasingly concentrated in living tissues as it moves up the food chain [39].

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In 1985, the U.S. EPA declared TCDD (2,3,7,8- Tetra chloro dibenzo dioxin) the most potent synthetic carcinogen yet tested. More recently, IARC has classified TCDD as known human carcinogen (Table 3.37). The U.S. EPA estimates that currently U.S. background dioxin exposures may result in upper-bound population cancer risk in the range of one in ten thousand to one in a thousand (one case of cancer out of 10,000 inhabitants or 1 case of cancer out 1000 inhabitants) [39].

Table 3.37. Effects of dioxins.

Cancer Classification	Toxic Effects		
	Developmental	Reproductive	Immune System
IARC (1997): 2, 3, 7, 8 TCDD: Group 1: carcinogenic to humans. Polychlorinated dibenzo-para-dioxins (other than 2, 3, 7, 8 TCDD): Group 3: unclassifiable as to carcinogenicity to humans. Polychlorinated dibenzofurans: Group 3: unclassifiable as to carcinogenicity to humans.	Humans: foetuses exposed via placenta and breast milk showed muscles reflexes and thyroids dysfunction. (WFPHA, 2000).	Humans: work exposure: <ul style="list-style-type: none"> • reduced level of sex male hormone testosterone. (WFPHA, 2000). Monkeys: (TCDD) chronic non toxic exposure: <ul style="list-style-type: none"> • reduction of reproduction rate. • Increased abortion. (WFPHA, 2000). 	Animals: suppression of cell-mediated and humoral responses, suggesting that both innate and acquired immunities can be targeted. (WFPHA, 2000).

Dioxins are known to be toxic at extremely low doses. In humans, there is evidence that high-level exposure to dioxins and furans can cause variations in serum lipid level, microsomal enzyme induction, and gastrointestinal alterations. Other studies of high-level occupational exposure have found associations with some types of cancer, and have concluded that in utero and lactational exposures to dioxins and furans are capable of affecting the hypothalamic/pituitary/thyroid regulatory system in human infants [39].

The World Health Organization recently lowered by more than half its tolerable daily intake from 10 pg, fixed previously in 1990, to 4 pg/kg bw, based on a recognition that subtle effects may already occur in the general population in developed countries at levels of 2 to 6 picograms. (WFPHA, World Federation of Public Health Associations, 2000) [39].

Because of their insidious, globe-trotting nature, dioxin is a global problem that needs a global solution [41].

3.7.8. Organotins

The group of chemicals known as the organotins is composed of a large number of compounds with differing properties and applications.

Organotins are organometallic complexes (compounds based on a metal atom – tin, attached to an organic molecule). They are a large class of compounds which differ in properties and applications. They can be divided into four groups of general formula:

- Mono-substituted Organotin Compounds ($R\text{SnX}_3$) - monomethyltins, monooctyltins, monobutyltins (MBT), monododecyltins;
- Di- substituted Organotin Compounds ($R_2\text{SnX}_2$) - dimethyltins, dioctyltins, dibutyltins (DBT), didodecyltins;
- Tri-substituted Organotin Compounds ($R_3\text{SnX}$) - triphenyltin acetate, triphenyltin hydroxide, tricyclohexyltin hydroxide, tributyltin (also referred to as TBT; the most common organotin in the marine environment).
- Tetra- substituted Organotin Compounds ($R_4\text{Sn}$) - tetrabutyltin (TTBT).

where R is usually an organic grouping and X an anion, e.g. chloride, fluoride, oxide, or hydroxide.

Organotins have widespread applications as:

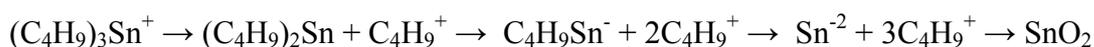
- Anti-fouling coatings for porous surfaces;
- Fungicides, herbicides, insecticides;
- Wood preservatives;
- Protectors of paper, textiles, leather, feathers and down;
- A disinfectant and as a molluscicide;
- Stabilizers in plastics, including polyvinyl chloride water pipes;
- Catalysts for polyurethane foam (as found in foam cushions).

The most commonly used are Tributyltin Oxide (TBTO) and copolymers of alkylacrylate-methyl methacrylate-TBT methacrylate. The latter is almost exclusively found in antifouling paint for ships while the former finds several uses though the majority is also used in antifouling paint. Other TBT compounds are the benzoate, acetate, laurate, maleate, naphthenate and phthalate esters and tributyltin chloride and fluoride. These TBT derivatives

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are manufactured in relatively small quantities and find commercial use as antimicrobials and catalysts.

Organotins can degrade in the environment due to ultraviolet radiation, biological degradation and chemical reactions that break down the tin-carbon bond. Partial mineralization was found for dioctyltin in standard biodegradation tests. Degradation depends on temperature and the presence of microorganisms. The process is by successive debutylation. That is the removal of all three organic butyl groups, one at a time.



Under aerobic conditions, organotins take one to three months to degrade, while in anaerobic these compounds will persist for more than two years. As anaerobic degradation is generally slow, the sediment can serve as a reservoir for organotins reentry into the water column and subsequent re-exposure to aquatic organisms.

- **Environmental fate**

After leaching out of the paint and into the water, TBT can be degraded (biological, hydrolysis, UV), it can partition into the sediment or it can be adsorbed (bioaccumulated) by aquatic organisms. All these interactions will affect the environmental concentration.

Studies in the field showed highest concentrations of organotins were near recreational boat marinas, largely because boats were freshly painted, launched and allowed to sit at the dock each year. Organotins are also present in areas with many ship movements, like harbours and ports. Effects from organotins are highly localized (to within a few km or less of the ports or harbors). In addition, on shipping lanes in the open sea, the toxic effects of organotins are observed.

Organotins-related risks are highest in enclosed harbors, marinas, anchorages and docking areas, especially where there is limited water circulation or flushing. Risks also are high in the waters and sediments adjacent to shipyards where ships with TBT coatings are cleaned and repainted.

- **Impact of organotins on marine environment**

Organotin compounds elicit toxicological properties depending on the nature and number of alkyl groups bonded to the tin atom. Organotins act on the mitochondria and chloroplasts of cells affecting ion exchange through membranes, inhibiting phosphorylation and ATPase activity (disrupt ATP synthesis), impair DNA/RNA production. TBT is highly attracted to fats and tends to be stored in these tissues. Generally, the larvae of species (oysters, mussels,

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crustaceans, molluscs, fish, and algae) are more sensitive to tributyltin exposure than are the adults.

The present use of TBT in antifouling paints causes TBT exposure to nontarget aquatic organisms such as mussels, clams, and oysters. TBT is very toxic to invertebrate marine life at very low dose levels and is thought to act primarily as an uncoupler.

This form accumulates in marine organisms, oysters being one of the worst affected organisms. The effects are such as deformities of the shell and decreased tissue growth.

Other forms of concern are the degradation products of TBT, dibutyltin and monobutyltin, and methyltins, which are formed in sediments by bacterial methylation.

Both phyto- and zoo- plankton is affected by TBT and this TBT can have toxic effects in concentrations down to ng/l level. In for example the organism dogwhelks TBT can cause "imposex", which means that females develop male sexual characteristics and become sterile. This in turn leads to devastating decreases of the population, even population collapse.

DBT is much less toxic and is considered to be more of an enzyme inhibitor

Tributyltin oxide (TBTO) is extremely toxic to aquatic life, and its use is being reduced in some countries. There are only limited exposure data [63].

TBTO is not genotoxic. One carcinogenicity study has been reported in which neoplastic changes were observed in endocrine organs, but the significance of these changes is considered questionable.

- **Organotin-regulations and their effects**

All of the organotins are now regulated by the "Organotin Antifouling Paint Control Act of 1988." This act regulates the use of these materials in paints and sets standards for the amount of biocides that can leach from the paint into water. A committee of the International Maritime Organization, meeting in early November, recommended that the use of anti-fouling boat bottom paint containing tributyltin, or TBT, be banned by 2008.

Since environmental concentrations of TBT have declined serious TBT pollution is now confined almost entirely to ports and harbours, especially those with dry docks where vessels are slipped and repainted. Since 1986 risks have declined to levels below that recommended by the US EPA for the protection of an aquatic community.

In addition to declining environmental TBT concentrations, the regulations for TBT use have been effective in the recovery of populations of sensitive animals.

3.8. Radioactive Pollution

Radionuclides are produced as fission products of heavy nuclei of such elements as uranium or plutonium. They also result from the reaction of neutrons with stable nuclei [3].

Radionuclides are formed in large quantities as waste products in nuclear power generation (reactors and nuclear power plants).

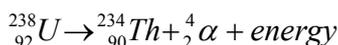
The sources of radioactive contamination which at the same time are the sources of disturbances in biological equilibrium are also:

- Radioactive fallouts caused by nuclear explosions and nuclear power station failures;
- Medical treatment (therapy) and diagnosis;
- Dial - plate of the clocks and compasses;
- Chemical radioanalysis;
- Flaw detection;
- Sterilization;
- Inscriptions indicating exit from cinemas;
- Use of radioactive material for the production of antyelectrostatic brushes for cleaning the records and cameras;
- Radon from chimneys.

With so many possible sources of radionuclides, it is impossible to entirely eliminate radioactive contamination of aquatic systems. Furthermore, radionuclides may enter aquatic systems from natural sources [3]. Brief description of radionuclides and their sources is presented in Table 3.38.

Radionuclides differ from other nuclei in that they emit ionizing radiation - alpha particles, beta particles, and gamma rays. The most massive of these emissions is the alpha particle, a helium nucleus of atomic mass 4, consisting of two neutrons and two protons and denoted ${}^4_2\alpha$. An example of alpha production is found in the radioactive decay of uranium-238 [3]:

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This transformation consists of a uranium nucleus, atomic number 92 and atomic mass 238, losing an alpha particle, atomic number 2 and atomic mass 4 to yield a thorium nucleus, atomic number 90 and atomic mass 234 [3].

Due to their large size, alpha particles do not penetrate matter deeply, but cause an enormous amount of ionization along their short path of penetration. Therefore, alpha particles present little hazard outside the body, but are very dangerous when ingested [3].

Beta radiation consists of either highly energetic, negative electrons, which are designated ${}_{-1}^0\beta$, or positive electrons, called positrons and designated ${}_{+1}^0\beta$. Although beta particles are more penetrating than alpha particles, they produce much less ionization per unit path length [3].

Gamma rays are electromagnetic radiation similar to X-rays, though more energetic. Gamma rays are much more penetrating than particulate radiation. Their degree of penetration is proportional to their energy [3].

Table 3.38. Radionuclides in water.

Radionuclide	Half-life	Nuclear Reaction, Description, Source
Naturally occurring and from cosmic reactions		
Carbon-14	5730 years	${}^{14}\text{N}(\text{n},\text{p}) {}^{14}\text{C}$, thermal neutrons from cosmic or nuclear-weapon sources reacting with N_2
Silicon-32	~ 300 years	${}^{40}\text{Ar}(\text{p},\text{x}) {}^{32}\text{Si}$, nuclear spallation (splitting of the nucleus) of atmospheric argon by cosmic-ray protons
Potassium-40	~ $1.4 \cdot 10^9$ years	0.0119% of natural potassium
Naturally occurring from ${}^{238}\text{U}$ series		
Radium-226	1620 years	Diffusion from sediments, atmosphere
Lead-210	21 years	${}^{226}\text{Ra} \rightarrow 6\text{steps} \rightarrow {}^{210}\text{Pb}$
Thorium-230	75 200 years	${}^{238}\text{U} \rightarrow 3\text{steps} \rightarrow {}^{230}\text{Th}$ produced in situ
Thorium-234	24 days	${}^{238}\text{U} \rightarrow {}^{234}\text{Th}$ produced in situ
From reactor and weapons fission		
Strontium-90	28 years	These are the fission-product radioisotopes of greatest significance because of their high yields and biological activity
Iodine-131	8 days	
Cesium-137	30 years	
Barium-140	13 days	The isotopes from barium-140 through krypton-85 are listed in generally decreasing order of fission yield.
Zirconium-95	65 days	
Cerium-141	33 days	
Strontium-89	51 days	
Ruthenium-103	40 days	
Krypton-85	10.3 years	

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Cobalt-60	5.25 years	From nonfission neutron reactions in reactors
Manganese-54	310 years	From nonfission neutron reactions in reactors
Iron-55	2.7 years	$^{56}\text{Fe}(n,2n)^{55}\text{Fe}$, from high-energy neutrons acting on iron in weapon hardware
Plutonium-239	24 300 years	$^{238}\text{U}(n,\gamma)^{239}\text{Pu}$, neutron capture by uranium

"This notation denotes the isotope nitrogen-14 reacting with a neutron, n, giving off a proton, p, and forming the isotope carbon-14; other nuclear reactions may be similarly deduced from the notation shown. (Note that x represents nuclear fragments from the spallation reaction.)"

Although it is possible that even the slightest exposure to ionizing radiation entails some damage, some radiation is unavoidably received from natural sources. For the majority of the population, exposure to natural radiation exceeds that from artificial sources.

Radionuclides having very short half-lives may be hazardous when produced but decay too rapidly to affect the environment into which they are introduced. Radionuclides with very long half-lives may be quite persistent in the environment but of such low activity that little environmental damage is caused. Therefore, in general, radionuclides with intermediate half-lives are the most dangerous. They persist long enough to enter living systems while still retaining a high activity. Because they may be incorporated within living tissue, radionuclides of "life elements" are particularly dangerous [3].

Radionuclides tend to spread through the whole ecosystem. They are toxic for all living organisms and accumulate in tissues and systems. Those elements which are uniformly distributed in the whole organism, such as: ^3H , ^{14}C or ^{24}Na , are less toxic. Much more toxic are those of radioisotopes which accumulate in the particular organ or tissue: radium (Ra), strontium (Sr) and thorium (Th) isotope, because they accumulate in bones and hemogenic organs, ^{131}I (iodine) in thyroid gland, ^{137}Cs (cesium) in muscles, ^{204}Th (thallium) in kidneys, ^{210}Po (polonium) in liver, ^{222}Rn (radon) in lungs.

There are isotopes listed in decreasing order of radioactivity:

^{90}Sr , ^{210}Po , ^{210}Pb , ^{223}Ra , ^{227}Ac , ^{227}Th , ^{228}Th , ^{230}U , ^{232}U , ^{233}U , ^{234}U , ^{242}Cm , ^{243}Cm , ^{244}Cm , ^{245}Cm , ^{246}Cm , ^{248}Cm , ^{124}I , ^{125}I , ^{126}I , ^{131}I , ^{133}I , ^{134}Cs , ^{137}Cs , ^{140}Ba .

Radiation damages living organisms by initiating harmful chemical reactions in tissues. Nuclear radiation accelerates the process of ageing of organism, causes mutagenic changes, tumours (of blood - leukaemia, skin, bones, large intestine), ulceration, necrotic changes of digestive system, skin and conjunctiva and failure of immune system (reduced immunity).

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Gonads, bone marrow, whole hemogenic system and tissues which undergo mitosis (division) are the most sensitive parts of a body to radioactivity.

Effects of nuclear radiation on the whole organism depend on the dose and absorbed dose rate, type of radiation, organism age and radiosensitiveness. Light is one of the factors that are to intensify the accumulation of some radionuclides in organisms. It was proved that marine and fresh - water plants much faster assimilate ^{60}Co in the presence of light. Also increase of temperature results in increased accumulation of radionuclides.

Studies of content of radionuclides in marine organisms, particularly in fish, are extremely important because they are one of the components of human diet. Variable content of radioactive substances in fish is dependent upon the environmental radioactivity, fish food, and growth stage: young fish assimilate strontium faster. Radioactive elements permeate through tissues, digestive tract and gills, both in passive and active way. Passive conversion takes place during equalization of the salt content between tissues and environment. Active one takes place as a result of ionic regulation in fish body. Radionuclides permeate mainly through gills. They can be also transferred through body surface and from food.

In biotic processes fish accumulate ^{90}Sr and ^{137}Cs present in water together with assimilation of calcium and potassium. The higher concentration of these elements, the lower assimilation of radioactive nuclides.

Strontium-90, a common waste product of nuclear testing, is a radionuclide of much concern. This element is interchangeable with calcium in bone. Strontium-90 fallout drops onto pasture and crop land and is ingested by cattle. Eventually, it enters the bodies of infants and children by way of cows' milk [3].

Some radionuclides found in water, primarily radium and potassium-40, originate from natural sources, particularly leaching from minerals. Others come from pollutant sources, primarily nuclear power plants and testing of nuclear weapons. The levels of radionuclides found in water typically are measured in units of picoCuries/liter (pCi/l), where a Curie is $3.7 \cdot 10^{10}$ disintegrations per second, and a picoCurie is $1 \cdot 10^{12}$ that amount, or $3.7 \cdot 10^{-2}$ disintegrations per second (2.2 disintegrations per minute) [3].

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