PESTICIDES, POLYCHLOROBIPHENYLS AND POLYCYCLIC AROMATIC HYDROCARBON RESIDUES AS CHEMICAL HAZARDS

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Hazards are the important parameters as far as safety of the food item is concerned. The hazards are generally classified into three categories namely, physical, chemical and biological and each one has a potential to cause adverse health effect. Chemical hazards are basically organic or inorganic compounds, pesticides, veterinary drugs, antibiotic residues, etc. and lot more are brought into the list of chemicals whose maximum residual limits are prescribed by buying countries. Chemical substances, in one form or other, cause health hazards to consumers. Some of these chemicals are derived from the ground in the case of plants and aquaculture products while certain other are caused by anthropogenic activities. Most often there are anthropogenic contaminants with ubiquitous distribution (Loganathan & Kannan, 1991; Reddy *et al.*, 1991). Extraordinary industrial development, rampant development of aquaculture and population explosion along the coastal belts contributed heavily to the ambient levels of pollution and environmental damage in the aquatic environment. Major form of pollutants comes from the urban wastewater, aquaculture and domestic sewage.

Pesticides

Pesticides are substances, or mixture of substances used in the control of pests viz. plant parasitic viruses, bacteria, nematodes, fungi, insects, weeds, rodents, and birds. Pesticides include all materials that are used to prevent, destroy, repel, attract, or reduce pest organisms and are extensively used in forestry, landscaping, agriculture, and domestic use. Even though pesticides are designed to kill or control particular living organism, indiscriminate or accidental misuse of these chemicals cause phenomenal effects in the ecosystem. Most of them are chemically stabile chemicals and are persistent in the environment. They are lipophilic in nature and hence have the tendency to get accumulated and magnified in the lipid fractions in the tissue.

Pesticides are in use for thousands of years. Some of the early demonstrations include burning sulphur in an attempt to control insects by Romans and the use of arsenic and pyrethrum by the Chinese. By the early 20th century, two classes of pesticides were primarily used

namely botanicals - natural chemicals derived from plant material, and inorganic salts. These were widely used as fungicides, herbicides and insecticides. The era of synthetic pesticides started with the discovery of DDT in 1934 (dichlorodiphenyltrichloroethane) and was a major breakthrough for agriculture development. Ever since innumerable preparations have been in use in the name of insecticides, fungicides, herbicides etc. However, excessive use of these chemicals led to banning of DDT in 1974 in most of the developing countries even though it is still used in most other countries.

It is estimated that about 2.5 million tons of pesticides are applied annually to control pest organisms. Most of this application is targeted on agricultural crops. Even though the use of pesticides had a very positive impact in the overall increase in food production, the risks associated with this include human health effects, livestock animal poisoning, beneficial insect losses, water contamination, wildlife losses, and the genetic evolution of pesticide resistance.

Classes of Pesticide

Pesticides are classified according to their chemical structure. Natural or organic pesticides are generally compounds extracted from plants. Many plants, like tobacco, chrysanthemum, and conifers, have evolved the ability to produce substances that are used for this purpose. Inorganic pesticides are poisons made from common natural highly toxic and indestructible chemicals like arsenic, copper, lead and mercury and hence can accumulate in the environment. Another class of chemicals is used to fumigate (Fumigants) the insects but due to the danger associated it has been banned world over.

The synthetic pesticides are broadly classed as follows:

Chlorinated hydrocarbons (DDT, chlordane, alrin, dieldrin, toxaphene, paradichlorobenzene, and lindane) are synthetic organic compounds commonly used in the past but have been removed from the market due to their environmental effects. DDT is very highly persistent in the environment, with a reported half life of between 2-15 years (USEPA,1989; Augustijn-Beckers, 1994) and is immobile in most soils. In Great Lake were the use of DDT was banned since 1970, the DDE accounted for more than 70% of the total DDD burden (Newsome & Andrews, 1993).

Organophosphates are 10 to 100 times more toxic than chlorinated hydrocarbons to animals larger than insects but are not persistent as chlorinate hydrocarbons. Parathion, malthion, dichlorvos, dimethyldichlorovinylphosphate (DDVP), and tetraethylpyrophosphate (TEPP) are some of the examples of this group.

Carbamate pesticides are derived from carbamic acid and kill insects in a similar fashion as organophosphate insecticides. They are widely used in homes, gardens and

agriculture. Like the organophosphates, their mode of action is inhibition of cholinesterase enzymes, affecting nerve impulse transmission. The signs and symptoms of carbamate poisonings are similar to those caused by the organophosphate pesticides. The carbamate's principal route of entry is either by inhalation or ingestion or secondarily through skin. They are very similar to organophosphates, and include such chemicals as carbaryl (Sevin), aldicarb (Temik), aminocarb (Zineb), carbofuran (Baygon), and Mirex.

Pesticides and the Environment

The pesticide reaches the ecosystem and gets part of the marine life and ultimately reaches the consumer. The presence of pesticides or their metabolites in low levels in the food is called "residue". The maximum level at which the pesticide do not produce any toxicological effect is called "Maximum residual limit". Up to 90 % of the pesticides applied never reach the intended targets. As a result, many other organisms sharing the same environment as the pests are accidentally poisoned. Contamination of groundwater and surface water by pesticides is a very common problem. Pesticides can contaminate aquatic systems by fallout from aerial sprays, soil erosion, or through the disposal or effluent from pesticide factories. Pesticides can enter water through surface runoff, leaching, or erosion.

Once the pesticide reaches the water system, its distribution and fate will depend on its persistence and solubility. Most pesticides that persist in a water system usually become adsorbed onto floating particles and settle out as sediment. Generally, the more persistent a pesticide is, the greater the effect it will have on the aquatic ecosystem. Also, the more soluble a pesticide is, the greater its potential is for aquatic system and groundwater contamination. Water composition, pH, temperature, aquatic life present and amount of suspended organic and inorganic material are some of the factors affecting the persistence of a pesticide in a water system. As a result of pesticide contamination of water both surface and groundwater, the organisms living in and using the water are affected. Compounds including lindane (γ-BHC), aldrin, heptachlor, chlordane, DDT and dieldrin have been extensively used in agricultural applications for control of insects and weeds (Hagan & Klumpp, 1995). As a result, these have been identified as contaminants in ground water, seawater, freshwater biota, freshwater and estuarine sediments and marine biota (Haynes *et al.*, 2004).

Habitat Alteration

Pesticides can also reduce the availability of plants and insects that serve as habitat and food for fish and other aquatic animals. Insect-eating fish can lose a portion of their food supply when pesticides are applied. A sudden, inadequate supply of insects can force fish to range farther in search of food, where they may risk greater exposure to predation. Aquatic plants provide as much as 80% of the dissolved oxygen necessary for aquatic life in ponds and lakes. Spraying herbicides to kill all aquatic plants can result in severely low oxygen levels and the suffocation of fish.

Ecological effects of pesticides

Pesticides are included in a broad range of organic micro pollutants that have ecological impacts. Different categories of pesticides have different types of effects on living organisms and hence generalization is difficult. Although terrestrial impacts by pesticides do occur, the principal pathway that causes ecological impacts is that of water contaminated by pesticide runoff.

Fish and aquatic animals are exposed to pesticides in three primary ways (1) direct absorption through the skin by swimming in pesticide-contaminated waters, (2) breathing, by direct uptake of pesticides through the gills during respiration, and (3) orally, by drinking pesticide-contaminated water or feeding on pesticide-contaminated prey. Exposure of fish and other aquatic animals to a pesticide depends on its biological availability (bioavailablility), bioconcentration, biomagnification, and persistence in the environment. The property of chlorinated hydrocarbon for bioaccumulation is strongly related to their capacity to bind to lipids. Bioavailability refers to the amount of pesticide in the environment available to fish and wildlife. Some pesticides rapidly breakdown after application while some others bind tightly to soil particles suspended in the water column or to stream bottoms, thereby reducing their availability. Some are quickly diluted in water or rapidly volatize into the air and are less available to aquatic life. The transformation of organic compounds directly from water column to the biota via gills or body surface into the circulatory fluids is called bioaccumulation or transferred via blood across the gastrointestinal tract in to the circulating fluid by a process called biomagnification (Connell, 1988). Bioconcentration is the accumulation of pesticides in animal tissue at levels greater than those in the water or soil to which they were applied. Some pesticides, such as DDT, are "lipophilic", and accumulate in, fatty tissue such as edible fish tissue and human fatty tissue. Less persistent and non stable pesticides get degraded and excreted from the system.. Biomagnification is a process where xenobiotic substances are transferred from food to organism resulting in higher concentrations compared with the source. Very high concentrations can be observed in top predators, including man.

In the organism, the chemical is transformed into a less toxic form and either excreted or stored in the organism. Different organs, especially the liver, may be involved, depending on the chemical. Enzymes play an important role in the metabolic process and the presence of certain enzymes, especially "mixed" function oxygenases (MFOs) in liver, is now used as an indicator that the organism has been exposed to foreign chemicals. The ecological effects of pesticides (and other organic contaminants) are varied and are often inter-related. The types of effects will vary depending on the organism under investigation and the type of pesticide. Cancers, tumours and lesions on fish and animals, reproductive inhibition or failure, suppression of immune system, disruption of endocrine (hormonal) system, cellular and DNA damage, teratogenic effects (physical deformities such as hooked beaks on birds) and higher concentration most often causes death of the organism.

Pesticides and aquatic life

Algae and sea grass tend to concentrate organochlorines to some extent and the major effect noticed is the decreased photosynthesis, respiratory inhibition or enhancement and growth reduction (Haynes and Johnson, 2000) through inhibition of cyclic phosphorylation and suppression of electron transport chain and ATP turn over (Ramachandran *et al,* 1984). Endrin, dieldrin and aldrin cause most toxic effects to aquatic plants even at concentrations lower than 1 $\mu g\ L^{-1}$ while DDT and DDE require slightly higher concentrations (Menzel et al., 1970; Powers *et al.*, 1975). Besides causing harmful effects on the metabolism in these plants they indirectly enters the fish and other forms of life and ultimately enters humans through fish and other aquatic lives.

The rivers, backwaters and ocean are the ultimate dumping place for all the pollutants, whether it is industrial effluents or agricultural runoffs. The chemicals thus enter the life of different organisms, big or small, habitat in the water. The toxicity of the pollutants depends on the physical and chemical parameters of water namely, pH, temperature, solubility, chelation with different metals and these have direct influence on the accumulation and biodisponibility for the target organisms (Chevreuil *et al.*, 1995). The accumulation of organochlorine compounds in fish is related to its lipid content, habitat, dietary intake, growth rate and metabolism (Pastor *et al.*, 1996). Muscle tissues from a wide range of fish species were found to contain organochlorine pesticides including chlordane, dieldrin and heptachlor epoixide (Roach & Runnie, 1990).

Among the different aquatic forms some mussels have the capacity to take in these chemicals and can act as biological markers. The blue mussels accumulate most hydrocarbons from polluted waters (Murray *et al*, 1991) and the zebra mussel, which is ubiquitary, and sedentary appears to do the job in freshwater environment (Murray *et.al*, 1991). The larger organisms accumulate pesticides in the body by bioconcentration and these in turn cause health hazards. Chlorinated pesticides (particularly DDT group of pesticides and lindane and chlorophenols were reported in eight of the fish samples anlaysed from Isipingo estuary, Natal, South Africa but were found to be with in the WHO prescribed limits (Grobler *et al*, 1996). Similarly about twenty-seven species of marine and freshwater fish from Cambodia were found to accumulate organochlorines with DDT and related pesticides predominating and that the freshwater fish had higher accumulation of pesticides suggested the possible contamination from watershed (Monirith *et al*, 1999). Bioaccumulation of these chemicals were related to the food habits as reported by their accumulation in higher concentrations in carnivorous fish sea mullet and the bottom feeder red mullet than the than in sea bass of Mediterranean region (Pastor *et al*, 1996). Seafood for human consumption has been contaminated with low levels of PCBs, DDT and its metabolites, chlordane compounds and lindane isomers (Kannan *et al.*, 1995). In Indian waters, 0.005 to 0.35-ppm level of pesticides have been detected in the Indian food fishes and shellfishes and were with in limits (Radhakrishnan et al, 1986; Radhakrishnan, 1994; Radhakrishnan and Antony, 1989).

Poly Chlorinated Biphenyls (PCB)

Polychlorinated biphenyls (PCBs) are a group of fat-soluble organic compounds with a biphenyl molecule, basically two benzene molecules attached together, with chlorine atoms attached at varying positions. They are oily liquids or solids, clear to light yellow in color, and with no smell or taste. PCBs are also known as arochlors and chlorodiphenyls. The PCBs are generally represented by a four-digit number. The first two digits represent the type of molecule and the second two digits the percentage makeup of chlorine in the molecule. For example, Arochlor-1242 and Arochlor-1254 contain 42 and 54 percent chlorine by weight, respectively (Moore and Ramamoorthy, 1984). PCBs are composed of 209 closely related compounds that differ from each other by the number and position of chlorine on the phenyl ring (Lee *et al.*, 2001).

PCBs have widespread industrial applications. At one time PCBs were common components of hydraulic fluids, lubricants, heat transfer fluids, and insecticides. PCBs were primarily manufactured as dielectric fluid for transformers and capacitors because of their ability to absorb heat, low flammability, low electrical conductivity, and favorable dielectric constant (Kennish, 1997). Currently, heat transfer fluids residing in old transformers and capacitors used in power distribution systems are the main sources of PCBs. Non-Liquid PCBs (NLPCBs) can be found in various items such as fluorescent light ballast potting material, ceiling tile coatings, and certain painted surfaces. However, due to its varied effects on health, U.S. stopped producing PCBs. As levels in the environment increased, the potential for harmful effects increased.

PCBs are generally liquid, viscous or viscous sticky resins. They are sparingly soluble in water and the solubility decreases with increasing chlorine content. They are stable compounds that break down very slowly in the environment. There are extensive reports available indicating the concentration of PCBs in the water resources throughout the world (Moore and Ramamoorhty, 1984; Armstrong *et al*, 1993; Kamman *et al* 1993; Sugiura *et al*, 1986; Grobler *et al*, 1996; Everaarts *et al.*, 1998; Pastor *et al*, 1996; Corsolini, 2000). PCBS enter the environment through many ways. They enter air as solid or liquid aerosol and remain there for longer time. In the process they get moved to other places. Through rain or snow they reach the water bodies and soil where they get adsorbed to soil particle and remain there for many years. Being sticky in nature gets adsorbed to particles in water and either moves down to the sediments or remains suspended. Inshore marine areas closer to industrial zones are often the highly polluted areas as far as PCBs are concerned. In the process, PCBs enter water plants and other living forms in water. As the proportion of dissolved portion of PCB is relatively low, their residual level in the plants and animals are also low. Zooplanktons are often associated with low residual levels than benthic species with exceptions being the association of high concentrations of PCBs in planktons with high lipid content.

PCBs can bioaccumulate in the fatty tissue of fish, birds, and mammals. The bioconcentration on depends not only on the concentration of these chemicals in the environment but also on the physiological and biochemical processes with in the organism concerned and these processes are species dependent (Pastor *et al*, 1996). From different experiments it was found out that mussels and benthic fish are the best indicators of coastal pollution in water and sediments (Porte and Albaiges, 1993). In most cases, the PCB concentrations are related to the high fat seasons (Moore and Ramamoorthy, 1984). As far as concentration in the body is concerned, maximum concentration is associated with fat deposits followed by liver and gonads (Loizeau, 1992).

The accumulation is by and large lowest in muscle and is related to the fat content. As PCBS are present in the atmosphere one get exposed to PCB by simple breathing particularly around electrical installation and dumping yards. It can also enter the system through contaminated drinking water or eating fish and other seafood, dairy products. If the mother is exposed to PCB it enters the offspring through the breast milk.

Exposures to PCBs over a long time may cause harmful effects to the skin (acne, rashes, and coloring of the nails and skin) and eyes (redness, burning, irritation, and discharge) and irritation in the nose. PCBs in the diet of animals produced similar effects. Repeated skin contact to PCBs in rabbits caused liver, kidney, and skin damage. Rats and other animals that breathed very high levels of PCBs over several months had liver and kidney damage. A single, large exposure to skin in rabbits caused death. Based on animal studies, Health and Human Services of USA has classed PCBs as potential even though their carcinogenic effect on humans is not fully confirmed. They are suspected human carcinogens and have been shown to be teratogenic (i.e., capable of inducing mutations in the offspring of affected organisms).

Toxicity

PCB concentration generally causes growth retardation at 10–100ppm levels while reduction in photosynthesis and carbon uptake are shown to occur at a still lower concentration of 0.1 – 1 ppb (Moore and Ramamoorthy, 1984). The toxicity varies with species of plant and invertebrates and also with the type of the arachlor. The fish are found to be sensitive to PCB. The normal reproduction was reported to be affected by exposure to PCB. The birds like waterfowl, effects similar to that produced by organochlorine pesticides, like reduction in eggshell thickness have been detected (Moore and Ramamoorthy, 1984).

The levels and residue profiles of contamination of polychloro biphenyls (PCB), polychloronaphthalenes (PCN), and chlorobenzenes (CBZ) in fish, moss, algae, sediment and water from the polluted river Krupa, Bela krajina, Slovenia, have been reported (Jan *et al*, 1994). Accumulation of PCB in the Zebra mussel was several folds higher than that of

other organochlorines (Chevreuil *et al*, 1996). PCB are reported in the fish samples from Isipingo estury, Natal, South Africa but were found to be with in the WHO prescribed limits (Grobler *et al,* 1996). PCBs constituted second highest pollutants after organochlorine pesticides in Cambodian fishes and were predominating in marine fish than in freshwater fish (In *et al*, 1999). Mediterranean red mullet were found to accumulate large concentrations of PCBs primarily due to their high lipid content (Pastor *et al*, 1996). As far studies with mammals are concerned the effects are almost similar to that produced by organochlorine pesticides. However, the severity is somewhat less compared to that of later. Besides the PCBs are known for their mutagenic properties

Regulations

	Environmental Protection Agency (EPA)	*Food and Drug Administration (FDA)*	*The National Institute for Occupational Safety and Health (NIOSH)*	*The Occupational Safety and Health Administration (OSHA)*
in lakes and streams	0.001 ppb			
in drinking water	< 4 mg/L for adults < 1 mg/L for children	----		
milk, eggs, other dairy products, poultry fat, fish, shellfish, and infant foods	---	no more 0.2-3 ppm		
workers not breathe air			0.001 mg/m^3 for a 10- hour workday	0.5 mg/m^3 (54 percent chlorine) or 1 mg/m^3 (42 percent chlorine) for an 8-hour workday

Pollutants like PCBs reach fat tissues through blood stream and get accumulate. As long as no metabolism of fat take place, the accumulation continues. When fat metabolism takes place as in the case of starvation, they reenter the blood stream and reach different tissues (Corsolini *et al.*, 2000). Recurrent cycles of accumulation and mobilization cause the organism high risk of toxic contamination. When a xenobiotic enters the system the hydrosoluble ones gets degraded by the mixed function oxygenase system and eliminated or converted in to less toxic materials while the fat-soluble portions accumulate in the adipose tissues (Corsolini, 2000).

Polycyclic aromatic hydrocarbons (PAH)

PAH refers to a large class of organic compounds containing two or more fused aromatic rings made up of carbon and hydrogen atoms. The general characteristics common to the class are solids, high melting- and boiling points, low vapour pressure, and very low water solubility, which tend to decrease with increasing molecular mass. PAH are chemically inert and soluble in many organic solvents and are highly lipophilic. These compounds are usually formed by the incomplete combustion and high temperature pyrolysis reactions like burning of coal, oil and other forms of organic matter. The largest emissions of PAH result from incomplete combustion of organic materials during industrial processes and other human activities.

PAH, especially these of higher molecular mass, entering the environment via the atmosphere are adsorbed onto particulate matter. The hydrosphere and geosphere are affected secondarily by wet and dry deposition. Creosote-preserved wood is another source of release of PAH into the hydrosphere, and deposition of contaminated refuse, like sewage sludge and fly ash, contributes to emissions of PAH into the geosphere. Little information is available about the passage of PAH into the biosphere. PAH occur naturally in peat, lignite, coal, and crude oil. Most of the PAH in hard coals are tightly bound within the coal structure and cannot be leached out. The release of PAH into the environment has been determined by identification of a characteristic PAH concentration profile, but this has been possible in only a few cases. Benzo [a] pyrene has frequently been used as an indicator of PAH, especially in older studies.

Motor vehicles are one of the major sources of PAH. The main compounds released from petrol-fuelled vehicles are fluoranthene and pyrene, while naphthalene and acenaphthene are abundant in the exhaust of diesel-fuelled vehicles. Although cyclopenta [cd]-pyrene is emitted at a high rate from petrol-fuelled engines, its concentration in diesel exhaust is only just above the limit of detection. The emission rates, which depend on the substance, the type of vehicle, its engine conditions, and the test conditions, range from a few nanograms per kilometre to 1000 mg/km. PAH emissions from vehicle engines are dramatically reduced by fitting catalytic converter devices.

Most PAHs entering the environment are formed unintentionally during burning (coal, oil, wood, gasoline, garbage, tobacco and other organic material) or in certain industrial processes. PAHs usually occur as mixtures of two or more PAHs and other chemicals. Bio magnification of PAH has not been observed in aquatic systems and would not be expected

to occur, because most organisms have a high bio-transformation potential for PAH. Organisms at higher trophic levels in food chains show the highest potential bio-transformation.

Both natural sources as well as anthropogenic activities contribute to the PAH in the environment. With industrial development, large quantities of PAH produced by anthropogenic activities are spread and have been detected in environment, water, soil and in livestock. Several of these compounds are suspected carcinogens even in low (μg/kg) concentrations.

PAH are compounds containing carbon and hydrogen and are generally non polar and aromatic. They are solids and sublimate slightly under normal conditions. Among the many PAH, only few are commercially produced and used. Naphthalene has got wide application in the manufacture of solvents, lubricants and dyes. It is also used in the production of moth repellent, insecticide, vermicide and intestinal antiseptic. Acenaphthelene and phenanthrene find their application as intermediates in plastics, dye and pesticide manufacture.

The PAH are broadly classified based on their properties in to two classes

- low molecular weight compounds containing 2 –3 rings aromatic, which include naphthalene, fluorene, phenanthrene and anthracene. These compounds are volatile to some extent and are relatively toxic to aquatic lives.
- Higher molecular weight compounds containing 4-7 aromatic rings, which include compounds from chrysene to coronene. These are not acutely toxic but are proven carcinogens.

The solubility of PAH being low in aqueous medium, they get adsorbed on the surface of particulate bodies and invariably sink to the bottom of the water bodies and get concentrated in the sediments. Hence, water contains generally low concentrations compared to aquatic lives and the sediments contain the highest magnitudes. PAH have generally low solubility in water due to their high molecular weight and low polarity but presence of anionic detergents increases their solubility in water. Low molecular weight PAH is depleted from the water bodies by volatalisation, microbial oxidation and sedimentation while high molecular weight ones are removed by photoxidation and sedimentation. Thus, more than 50% of naphthalene gets vaporized from water depending on water temperature. Photolysis of PAH takes place through the presence of atmospheric oxidants. SO_2 oxidises PAH in to quinines, which are reported to be highly carcinogenic. About 60% of benzo (a) pyrene gets oxidized by light while certain others have little or no effect. HO-radicals and ozone are primary contributors to photoxidation.

Chemistry of some of the common PAH

Name	Formula/M.wt	Crystal, colour	m.p.
Anthracene, (An)	$C_{14}H_{10}$/178.23	plates, colourless	218
Benzo (a)anthracene, (B(a)A)	$C_{18}H_{12}$/ 228.9	plates, greenish yellow	160.5 - 1
Benzo (b) fluoranthene, (B(b)F)	$C_{20}H_{12}$/252.39	Needles,colourless	167-168
Benzo (k) fluoranthene, (B(k)F)	$C_{20}H_{12}$/252.32	Yellowish needles	217-217.
Benzo (g,h,i) perylene, (B(g,h,I)P)	$C_{22}H_{12}$/276.34	plates, yellowish green	277 – 27
Benzo (a) pyrene, (B(a)P)	$C_{22}H_{12}$/252.30	Yellowish needles	179.9 – 1
Benzo(e) pyrene, (A(e)P)	$C_{20}H_{12}$/252.31	Reddish pillars	178 – 17
Chrysene, (Chry)	$C_{18}H_{12}$/228.29	Plates reddish violet Fluorescence	254
Coronene, (Cor)	$C_{24}H_{12}$/300.36	Yellow needles	442
Dibenzo (a,h) anthracene, DB(a,h)A)	$C_{22}H_{14}$/278.35	Silver leaves	269 – 27
Dibenzo(a,h)pyrene (DB(a,h)P)	$C_{24}H_{14}$/302.37	Goldfish-organge plates	315
Dibenzo(a,i)pyrene (DB(a,i)P)	$C_{24}H_{14}$/302.37	Yellowish-organge plates	281.5 - 2
Fluoranthene,(Flu)	C_6H_{10}/ 202.26	Colourless needles/ plates	110.4-11
Phenanthrene, (Phe)	$C_{14}H_{10}$/178.23	White plates	100.7 – 1
Pyrene, (Py)	$C_{16}H_{10}$/202.26	Yellow plates	156

Metabolism of PAH

Microorganisms present in water, sewage, soil, sediments and soil have capacity to degrade PAH. In bacteria PAH are oxidised to dihydrodiols and then to catechols before finally getting oxidised to carbon dioxide and water. In the bacterial pathway cis-dihydrodiol is produced through a dioxetane intermediate, whereas in the mammalian microsomal system a trans-dihydrodiol is produced through an arene oxide intermediate, which appear to be responsible for the carcinogenicity or mutagenicity of some PAH. Rate of PAH degradation tends to decrease with increasing PAH molecular weight. Bacterial populations from oil-contaminated areas metabolize PAH more readily than populations from clean areas. Fungi metabolize PAH in a way somewhat similarly to mammalian microsomal system.

In mammals, the enzyme system cytochrome P-450-dependent mixed function oxidase, mixed-function oxygenase (MFO), aryl hydrocarbon hydroxylase or drug-metabolizing system are responsible for the metabolism of organic compounds, such as PAH. Certain PAH may be transformed to intermediates that are highly toxic, mutagenic or carcinogenic to the

host. Metabolic activation by the MFO system is a prerequisite for PAH-induced carcinogensis and mutagenesis. In invertebrates, MFO activity seems to be restricted to some members of arthopoda and annelida. MFO activity has been detected in some crustacean species, which produce PAH metabolites very rapidly. The types of PAH metabolites produced by marine and freshwater animals are similar to those produced by mammals. In fish, as in mammals, most MFO activity is localized in the liver, also there areactivities in gills and kidney. Exposure to PAH or petroleum results in rapid induction of MFO activity in some aquatic species.

PAH Residues

Major routes for PAH into marine and fresh waters include biosynthesis, spillage and seepage of fossil fuels, discharge of domestic and industrial wastes, fallout or rainout from air, and runoff from land. Spillage and seepage of petroleum is the main source of PAH in the waters.

Most of the environmental PAH remain relatively near their point origin, and PAH concentrations decrease approximately logarithmically with distance from the source. Most of the PAH entering the aquatic environment are localized in rivers, estuaries, and coastal marine water. Since PAH are less sensitive to photooxidation in water than in air, they are more persistent in the aquatic environment. PAH enter water, are quickly adsorbed on particulate matter, and large amounts are deposited in bottom sediments. Relative concentrations of PAH are generally highest in the sediments, intermediate in aquatic biota and lowest in the water column. Routes of removal of PAH from the aquatic environment include volatilization from water surface, photooxidation, chemical oxidation, microbial metabolism and metabolism by higher metazoans.

PAH being non-polar and hydrophobic, they exhibit relatively low aqueous solubility. Solubility also decreases as the number of rings increases. PAH are slightly less soluble in seawater than in fresh water.

Effects on humans

PAH, being soluble in fat gets accumulated in adipose tissue and liver. These though not directly implicated in the induction of cancer, they are either known or suspected carcinogen and contribute to carcinogenic pressure in people. Besides, PAH are implicated in damage to hematophorotic and lymphoid systems. Degeneration of the spleen, thymus and mesenteric lymph nodes and inhibition in the development of bone marrow has also been observed.

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