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Environmental Effects of Polycyclic Aromatic Hydrocarbons

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Abstract

Polycyclic aromatic hydrocarbon (PASHs) are a class of unique compound that consist of fused conjugated aromatic rings and do not contain heteroatoms or substituents carrier. These compounds can be point source (e g, oil spill) or non-point source (e.g; atmosphere deposition) and are one of the most widespread organic pollutants. Some of them are known or suspected carcinogens and are linked to other health problems. They are primarily formed by incomplete combustion of carbon-containing fuels such as words, coal; diesel; fat, tobacco or incense etc. PAHs exert there toxicity following biotransformation to toxic metabolites, which can be bound covalently to cellular macromolecules such as protein, DNA and RNA, which causes cell damage, mutagenesis and carcinogenesis. However, during biological and chemical degradation of PAHs other toxic compound may be formed. If these transformation products are sufficiently persistent they could potentially accumulate during remedial processes. This will provide the background information and rationale for the derivation of distribution behaviour, environment contaminations, sources, types, the effect of PAHs on the environment and the recommendations.

Keywords : Environment, deoxyribonucleic acid, polycyclic aromatic hydrocarbons, ribonucleic acids and toxicity.

INTRODUCTION

The term Polycyclic aromatic hydrocarbons (PAHs) also known as Poly-aromatic hydrocarbons or polynuclear aromatic hydrocarbons are a class of organic chemical consisting of two or more fused aromatic rings and do not contain heteroatom or carry substituents (Fetzer, 2000). PAHs belong to the group of persistent organic pollutants (POPs). These are organic pollutant contaminants that are resistant to degradation, can remain in environment for a long period and have the potential to cause adverse environmental effects (Jaarsveld et al., 1997). As a pollutant, they are at concern because some compounds have been identified as carcinogenic, mutagenic and teratogenic (ECSC, 2002). PAHs usually occur naturally, but they can be manufactured as individual compounds for research purposes, however, not as the mixtures found in combustion product (ES/I-ES/7, 1983). PAHs also occur in oil, coal, and tar deposits, and are produced as by product of fuel burning (whether fossil fuel or biomass) (Fetzer, 2000). Naphthalene is the simplest example of a PAH (ECSC. 2002). They can have a faint, pleasant odor (Malisezewska-Kordybach, 1998). A few PAHs are used in medicines and to make dyes, plastic and pesticides (Wania et al 1996). Over 100 compounds existing in indoor air have been identified to date, two of the more common ones are benzo (a) pyrene and naphthalene (Malisezewska-Kordybach , 1998).

Environment:

Environment is defined as the totaling of circumstance surrounding an organism or group of organisms especially, the combination of external physical conditions that affect and influence the growth, development and survival of an organism [ECSC. 2002]. It consist of flora, fauna and the abiotic and includes the aquatic, terrestrial and atmospheric habitats (Lipniak et al.,1994). The environment is considered in terms of the most tangible aspects like air, water, soil and food. The less tangible, though no less important the communities we live in (Lipniak et al., 1999).

Table 1: Chemical Characteristics of the Ten Monitored PAHs

PAHs	Chemical Formula	Molecular weight	Water solibility,Mg/L	Log KOW	Log KOC
				3.37	2.97
Naphthalene	C10H8	128	31.69	4.07	1.40
Acenaphthylene	C12H8	152	3.93	3.98	3.66
Acenaphthene	C12H10	154.21	3.93	4.18	3.86
Fluorene	C13H10	166.2	1.68-1.98	4.45	4.15
Phenanthrene	C14H10	178.2	1-1.6	4.45	4.15
Anthracene	C14H10	78.2	0.0446	4.90	4.58
Fluoranthene	C16H10	202.26	0.206	4.88	4.58
Pyrene	C16H10	202.3	0.129-0.165	5.61	5.30
Chrysene	C18H12	228.3	0.0015-0.0022	6.04	5.74
Benzo(b)fluoranthene	C20H12	252.3	0.0012		

Sources: Futoma et al., 1981; Tiehm et al., 1997;Verschueren ,1983 and ATSDR,1993).

ENVIRONMENTAL CONTAMINATIONS:

Environmental contaminations are introduced into water, air and soil of microorganisms, chemical, toxic substances, wastes or waste water in a concentration that makes the medium (air, water and soil) unfit for its next intended use (consumption, crop production, in-habitation) [Environment 1998]. OR Environmental contamination is the pollution of environment which causes discomfort, instability, disorder and leaves harmful impact on the physical system and on living organism (Environment 1998).

Contamination can take the form of chemical substance, or energy such as noise, heat etc. The element of contamination can be foreign substance or energies or naturally occurring, they are considered contaminants when they exceed natural level (Environment 1998).

With the increasing awareness day by day about environmental degradation and pollution, the field of ecology has become an entirety in itself (Kawamura et al 1994). The pace with which this stream of environmental science has progressed has invented a lot of newer terms with meanings totally unrelated to the common words (Paterson et al 1989). Ecology is all about how environment is maintained, degrades and destroyed by man and the various harmful effect that can be associated with the ecological imbalance (Paterson et al 1989). The gravity of this ecological imbalance has been well understood by the ecologist, one of the consequences of this is the emergence of terminologies in the science of ecology (ATSDR 2010).

TYPES OF CONTAMINATIONS

1. AIR CONTAMINATIONS

Air contamination is the human introduction into the atmosphere of chemical, particulate matter, or biological materials that causes harm or discomfort to human or other living organisms or damages the environment [ATSDR 2010]. Air contamination is often identified with major stationary sources, but greatest source of emission is mobile source, mainly automobiles (Peter, 2003]. Also atmosphere contamination can occur when chemical companies or other businesses are releasing noxious fumes into the environment and are thus inhaled by the people in that area (Paterson et al 1989).

2. WATER CONTAMINATIONS

Water contamination is the pollution of water bodies such as lakes, river, oceans, and ground water caused by human activities which can be harmful to organisms and plant which live in these water bodies (Sims et al 1983). Like contamination of underground usually arises when individuals have deep wells. In those circumstances, the ground aquifer is contaminated with the specific chemical or chemical released by the responsible party (Falex 2005). This materials then develops into a plume and infiltrates the various well water sources. Individuals that own the wells are then exposed to the chemical by ingestion (drinking), skin contact (bathing) and inhalation (breathing steam from the water). Water contamination has many causes and characteristics. The primary source of water contamination are generally grouped into two categories based on their point of origin (Paterson et al 1989).

* Point – source contamination refers to contaminants that enter a water way through a discrete point source.

* Non-point source, refer to contamination that as its name suggests does not originate from a single discrete source (Ellenhorn , 1988).

3. SOIL CONTAMINATIONS

Another type of contamination is soil contamination. This type of contamination typically arises from the rupture of underground storage tanks, application of pesticides, percolation of contaminated surface water to subsurface strata, oil, fuel, dumping, leaching of wastes from landfills or direct discharge from industrial waste to the soil (Environment 1998). When areas flood, heavy metals and chemicals are deposited in the environment and thus contaminate the soil (Sims et al 1983). There is a very large set of health consequences from exposure to soil contamination depending on pollutant or contaminant type (Environment 1998).

SOURCES OF CONTAMINATIONS

While it would be impossible to list all the potential source of chemical contamination. The following list will serve to illustrate typical contaminations sources:-

- Gas stations.
- Machine shops.
- Rail and yard and other rail road – related work site.
- Chemical manufacturing plants.
- Incinerators.
- Chemical waste storage facilities.
- Oil refineries.
- Landfills.
- Automobile engine (Osu et al 1990).

POLYCYCLIC AROMATIC HYDROCARBONS (PAHS)

The major environmental concerns in urban and industrial areas are Polycyclic aromatic hydrocarbons. They have a relatively low solubility in water, but are highly lipophilic (Sim et al, 1983). When dissolved in water or absorbed on particulate matter, PAHs can undergo photodecomposition when exposed to ultraviolet light from solar radiation (Osu et al,1990). In the atmosphere, PAHs can react with pollutants such as ozone, nitrogen oxides and sulphur dioxides, yield diones, nitro – and dinitro- PAHs and sulphonic acids, respectively (Kawamura et al 1994). PAH may also be degraded by some microorganisms in soil (Sims et al 1983). PAHs pollutants have high molecular mass, PAHs of 4 and more condensed aromatic rings are considered to be more dangerous than 2 and 3 rings PAHs in view of their potentials (Kawamura. et al, 1994).

The movement of PAHs in the environment depends on properties such as how easily they dissolve in water and how easily they evaporate in the air. (Jaarsveld et al 1997). As persistent organic pollutants (POPs), some of them are susceptible to dispersion on a global scale because in addition to having environmental persistence, they move between the atmosphere and earth's surface in repeated, temperature-driven cycles of deposition and volatilation (Jaarsveld et al 1997). POPs are truly multimedia contaminants which occur in all parts of the environment: atmosphere, inland and sea water, sediments, soil and vegetation (Paterson et al 1989, Environment 1998 , Jaarsveld et al 1997). They are mainly of authropogenic origin and have no significant natural sources (Fetzer, 2000). PAHs (which are known for their strong mutagenic, carcinogenic and toxic properties) are composed of carbon and hydrogen atoms arranged in the form of fused benzene rings (Sims, et al 1983). There are thousands of PAHs compounds in the environment but in practice PAHs analysis is restricted to the determination of 6 to 16 PAHs as priority pollutants, while some of these, e.g. benzo (a) pyrene, chrysene, benzo (a) anthracene are considered to be potential human carcinogens (Fig. 1). PAHs are the most toxic among the hydrocarbon families (Catoggio, 1991). Individual PAHs differ substantially in their physical and chemical properties (Malisezewska-Kordybach, 1998). The widespread occurrence of PAHs is largely due to their formation and release in all processes of incomplete combustion of organic materials. The last century of industrial development caused a significant increase of PAHs concentrations in the natural environment (Wania, 1996, Wild et al 1995).

Investigation in the content of PAHs in ice cores from Greenland showed that the present level of these compounds is about 50 times higher than in preindustrial periods which changes in their qualitative distribution , suggest that the sources of PAHs shifted from biomass burning to fossil fuel combustion in the last 200 years . The general trends in PAHs concentration in the ice core were in agreement with the historical record of world Petroleum production (Kawamura et al 1994).

Polycyclic aromatic hydrocarbons reveal their toxicity following biotransformation to toxic metabolites (Varanasi, et al 1991) through metabolic activation (one-or two-electron oxidation) in the organism (Cavalieri, 1985). As defined by the international union of pure and applied chemistry (IUPAC), the simplest PAHs are phenanthrene and anthracene. PAHs may contain four-, five-, six-, or seven- membered rings, but those with five or six are most common. PAHs comprised only of six-membered rings are called alternant PAHs. Certain alternant PAHs are called benzenoid PAHs. PAHs containing up to six fused aromatic rings are often known as small PAHs and those containing more than six aromatic rings are called large PAHs (Pure Appl Chem 2009), 296 Tuvikene: Responses of fish to PAHs • ANN. ZOOL. FENNICI Vol. 32

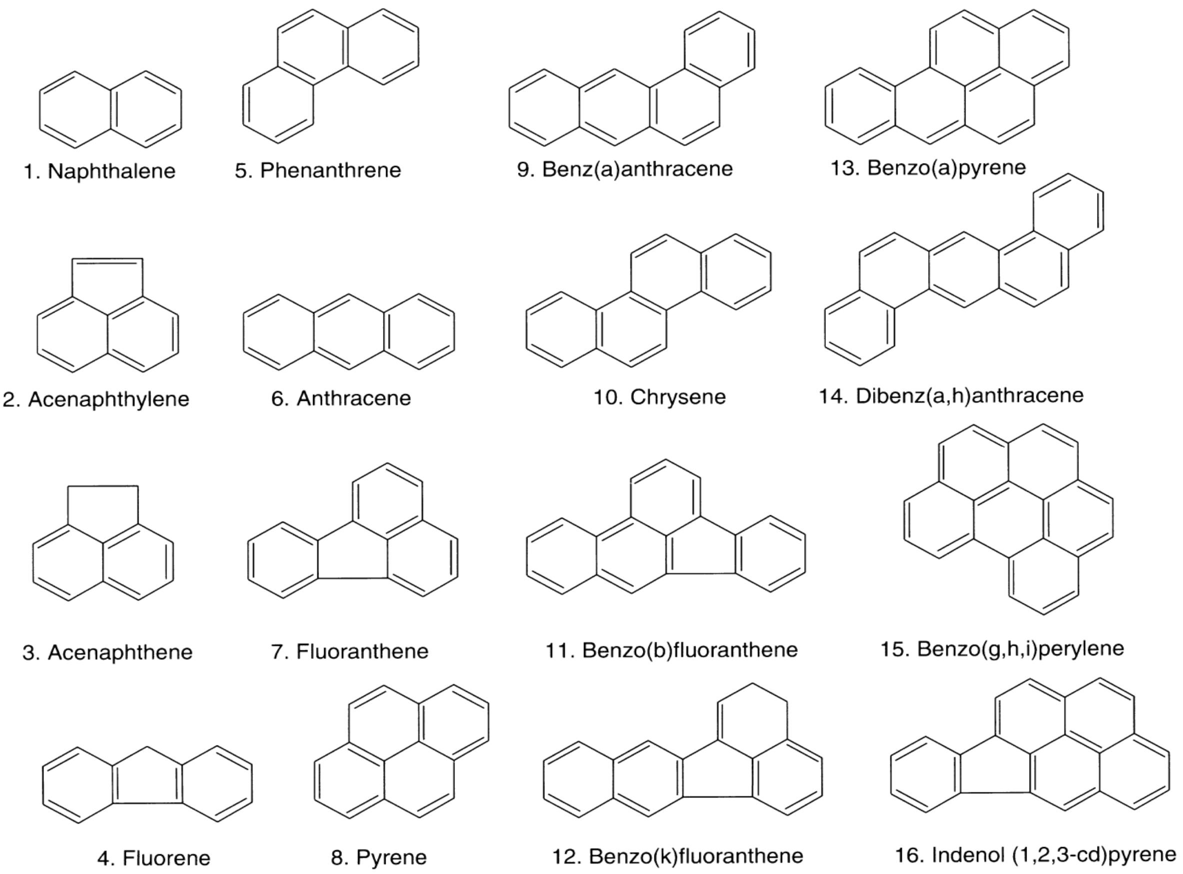
1. Naphthalene
5. Phenanthrene
9. Benz(a)anthracene
13. Benzo(a)pyrene
2. Acenaphthylene
6. Anthracene
10. Chrysene
14. Dibenz(a,h)anthracene
3. Acenaphthene
7. Fluoranthene
11. Benzo(b)fluoranthene
15. Benzo(g,h,i)perylene
4. Fluorene
8. Pyrene
12. Benzo(k)fluoranthene
16. Indenol (1,2,3-cd)pyrene

Fig. 1. Structure of sixteen polycyclic aromatic hydrocarbons as US Environmental Protection Agency (EPA) and World Health Organisation (WHO) priority pollutants.

SOURCES OF PAHS

Polycyclic aromatic hydrocarbons are lipophilic, meaning they mix more easily with oil than water. The larger compounds are less water – soluble and less volatile (i.e less prone to evaporate) (Glenn, 1995). Because of these properties, PAHs in the environment are found in soil, sediment and oily substances, as opposed to in water or air (Glenn , 1995). Natural crude oil and coal deposits contain significant amount of PAHs, arising from chemical conversion of natural product, molecules such as steroids to aromatic hydrocarbons [Glenn, 1995]. They are also found in processed fossil fuel, tar and various edible oils (Glenn, 1995). Smoke has a lot of PAH (Wania et al,1996). Indoor household source of PAHs include cigarette/tobacco smoke, smoldering fire places, wood stoves, unwanted gas burning appliances, kerosene space heaters, and the charring or burning of food (EPA, 2001). PAHs are one of the most widespread organic pollutant, in addition to their presence in fossil fuel they are also formed by incomplete combustion of carbon-containing fuel such as wood, coal, diesel, fat and incense (BBC News, 2001). Different types of combustion yield different distributions of PAHs in both relative amount of individual PAHs and in which isomers are produced (Glenn, 1995). Thus coal burning produces a different mixture than motor fuel combustion or a forest making the compounds potentially useful as indicator of burning history (BBC News, 2001).

Natural source include release in forest fire and from volcanic eruptions. Most environmental PAHs are products of incomplete combustion or pyrolysis of fossil fuel (Ellenhorn et al, 1988; ES/I-ES, 1983). The stationary fuel sources are responsible for over 97% of PAHs emissions (Pike, 1992). The study of this compounds is due mainly to their carcinogenic and widespread occurrence in environmental components, including surface soil (ES/I-ES, 1983.). Most of the PAHs are introduced into the soil from atmospheric decomposition after local and long-range transport, which is supported by the presence of PAHs in soil of regions remote from any industrial activity (Thomas, 1986). Other potential sources of PAHs in environment include disposal from public sewage treatment, irrigation with coke oven effluent, leachate from bituminous coal storage sites, and use of soil compost and fertilizers (Santodonato , et al 1981).

PAHs are produced in all processes of incomplete combustion of organic substance (Sims 1983; Wild et al 1995; Menzie et al 1992). Their production is favoured by an oxygen deficient flame, temperature in the range of 650^0C – 900^0C and fuel which are not highly oxidized. Natural sources of pyrogenic PAHs such as volcanic activity and forest fire do not significantly contribute – for the present – to overall PAHs emissions (Sims et al 1983; Ellenhorn 1988, Wild et al 1995). Anthropogenic source can be devised into two categories: combustion of material for energy supply (e.g. coal, oil, gas, wood etc) and combustion for waste minimalization (e.g waste incineration) (Wild et al 1995; Bakowski . et al 1988; Ramdahl et al 1983). The first category include stationary source like industry (mainly coke and carbon production, petroleum processing, aluminium sintering etc), residential heating (furnaces, fire places and stoves, gas and oil burner), power and heat generation (coal, oil, wood and peat power plant) and mobile sources like (car, lorries, trains, air planes) and sea traffic (gasoline and diesel engines) (Wild et al 1995).

Second category covers incineration of municipal and industrial waste. Other miscellaneous sources contain unregulated fire such as agricultural burning, recreational fire, crematoria, etc (Wild et al 1995; Bakowski. et al 1988; Ramdahl et al 1983).

USES OF PAHS

PAHs are not synthesized chemically for industrial purposes [DHGSA 1984]. Rather than industrial sources, the major services of PAHs is the incomplete combustion of organic material such as coal, oil and wood. However, there are few commercial uses of many PAHs. They are mostly used as intermediaries in pharmaceutical, agricultural product, photographic products, thermosetting plastic, lubricating materials, and other chemical industries [ATSDR 2010]. General uses are:-

Table 1: Summary of some PAHs and their uses. (ATSDR, 2010).

PAHs	Uses
Acenaphthene	Manufacturing of dyes, plastic, Diluents, pharmaceuticals and pesticides and processing of certain foods.
	Manufacture of dyes, pigments, and diluents for wood preservatives.
Anthracene:	It is used in the manufacture of some dyes and the wood preservation creosote
Chrysene	Manufacture of dyes, pharmaceuticals, and agrochemicals
Fluorene	It is used as a fumigant in households, soil museum etc to repel moths/insects attacks
Naphthalene.	Manufacture of Pesticides, and resins
	Manufacture of pigments
Phenanthrene	
Pyrene:	

Other PAHs may be contained in asphalt used for the construction of roads, as well as roofing tar. (ATSDR 2010). Precise PAHs, specific refined products are used also in the field of electronics, functional plastic and liquid crystals (Peter, 2003).

EFFECTS OF PAHS

1. ENVIRONMENTAL EFFECTS

PAHs are usually released into the air, or they evaporate into the air when they are released to soil or water (INCHEM 2010). PAHs often adsorb to dust particles in atmosphere, where they undergo photo oxidation in the presence of sunlight, especially when they are adsorbed to particles. This oxidation process can break down the chemical over a period of days to week (Santodonato, 1981). Since PAHs are generally insoluble in water, they are generally found adsorbed on particulate and precipitated in the bottom of lakes and rivers, or solubilized in any oily matter which may contaminate water. Sediments, and soil, mixed microbial population in sediment/water system may degrade some PAHs over a period of weeks to months (ATSDR 2010).

The toxicity of PAHs is affected by metabolism and photo-oxidation, and they are generally more toxic in the presence of ultraviolet light. PAHs have moderate to high acute toxicity to aquatic life and birds. PAHs in soil are unlikely to exert toxic effect on terrestrial invertebrates, except when soil is contaminated (Peter, 2003).

Adverse effects on these organism include tumors, adverse effects on reproduction, development and immunity, mammals can absorb PAHs by various routes e.g. inhalation, dermal contact and ingestion (ATSDR 1993).

Plant can absorb PAHs from soils through their roots and translocate them to other plant parts . Uptake rates are generally governed by concentration, water solubility and their physicochemical state as well as soil type. PAH – induced phytotoxic effect are rare. Certain plant contain substances that can protect against effect, whereas other can synthesize PAH that act as growth hormones (ATSDR 2010).

PAHs are moderately persistent in the environment, and can bioaccumulate. The concentration of PAHs found in fish and shell fish are expected to be much higher than in the environment from which they are taken. Bioaccumulation has been also shown interrostrial invertebrates, however PAHs metabolism is sufficient to prevent biomagnification (Borosky, 1999).

Table 2 :Summary on some PAHs found in some food samples

FOOD SAMPLES	PAHs FOUND	Reference
Baby food and Processed Cereal	Benzo(a)Pyrene, Chyrsene, enzo(a)anthrance ,Benzo(e)Pyrene,bezo(g,h,i)perylene, Phenanthrene.	(FSAI, 2006)
Chocolate	Benzo(a)pyrene, Chyrsene, anthracene, cyclopenta(c,d)pyrene, benzo(a,h)anthracene Phenanthrene, Benzo(e)Pyrene ,coronene.	(FSAI, 2006)
Fish and shell fish	Naphthalene, Flourene, Pyrene, Phenathrene, Acenahthene, acenaphthalene, 2-methy naphthalene, Benzo(a)pyrene, chyrsene, anthracene , Dibenzo(a,h)anthracene.	(Igwe et al., 2011)
Fruit	Naphthalene, Flourene, Pyrene, Phenathrene, Acenahthene, acenaphthalene, Benzo(a)pyrene, cyrsene, anthracene , Dibenzo(a,h)anthracene, fluoranthene.	(FSAI, 2006)
Vegetables (Carrots and potates)	Naphthalene, Flourene, Pyrene, Phenathrene, Acenahthene, acenaphthalene, Benzo(a)pyrene,anthracene, Dibenzo(a,h)anthracene, fluoranthene, Benzo(b,j,k)flouranthene, inden(1,2,3-cd)pyrene, Benzo(g,h,i)perylene	(Danish EPA , 2000)
Carbohydrates	Pyrene, Phenathrene, Acenahthene, Benzo(a)pyrene Benzo[b,j,k]fluoranthene , Benzo(a)anthrance .	(Pies, 2008)
Meat	Naphthalene, Benzo[g,h,i]fluoranthene, Flourene, Pyrene, Phenathrene, Acenahthene, acenaphthalene,2-methynaphthalene, Benzo(a)pyrene, cyrsene, anthracene, benzo(a,h)anthracene .	(FSAI , 2006)
Coffee, Tea, cocoa	Benzo(a)anthrance,Naphthalene,Pyrene Benzo(a)fluoranthene, inden(1,2,3-cd)pyrene , Benzo(a)pyrene, Dibenzo(a,h)anthracene ,perylene, anthrance.	(Santino et al.,2009)
Seafood (Crayfish)	Naphthalene, Flourene, Pyrene, Phenathrene, Acenahthene, acenaphthalene, 2-methy naphthalene, Benzo(a)pyrene, cyrsene, anthracene	(FSAI , 2006)

HEALTH EFFECTS

1. ACUTE OR SHORT-TERM HEALTH EFFECTS.

The effects on human health will depend mainly on the length and extend of exposure, the amount or concentration of PAHs one is exposed to, and of course the innate toxicity of the PAHs, and whether exposure occurs via inhalation ingestion or skin contact. A variety of other factors can also affect health impacts, including subjective facts such as pre-existing health status and age (Collins,1998).

The ability of PAHs to induce short-term health effects in human is not clear. Intake of PAHs from contaminated soil occur via ingestion, inhalation or dermal (skin) exposure to contaminated soil/dust and from inhalation of PAH vapours. Tilling the dry soil can result in ingestion of small but measurable amount of soil. Occupational exposure to high level of pollutant mixture containing PAH has resulted in symptoms such as eye irritation, nausea, vomiting, diarrhea and confusion (Collins, et al 1998).

However, it is not known which components of the mixture where responsible for the effect and other compounds commonly found with PAHs may be the cause of these symptoms.

2. Chronic or Long-term Health Effects

Health effect from chronic or long-term exposure to PAHs may include decrease immune function, cataract, kidney and liver damage (e.g. jaundice), breathing problems, asthma like symptoms and lung function abnormalities and repeated contact with skin may induce redness and skin inflammation. Naphthalene, a specific PAH, can cause the breakdown of red blood cell if inhaled or ingested in large amounts (Collins, et al 1998). If exposed to PAHs, the harmful effect that may occur largely depend on the way people are exposed (BBC News 2001).

3. Carcinogenicity

Although unmetabolized PAHs can have toxic effect, a major concern is the ability of the reactive metabolities, such as epoxides and dihydrodiols, of some PAHs to bind to cellular proteins and DNA. The resulting biochemical disruption and cell damage leads to Mutations, developmental malformation, tumors, and cancer. Evidence indicates that mixtures of PAHs are carcinogenic to humans (Grimmer, et al 1988). The evidence came primarily from occupational studies of workers exposed to mixtures containing PAHs and those long-term studies have shown an increase in risk of predominantly skin and lung, but as well as bladder and gastrointestinal cancers. However, it is not clear from these studies whether exposure to PAHs was the main cause as workers were simultaneously exposed to other cancer – causing agent (e.g. aromatic amines) (Grimmer, et al 1988).

Animals exposed to level of some PAH over long period in laboratory studies have developed lung cancer from inhalation, stomach cancer from ingesting PAHs in food and skin contact. Benzo (a) pyrene is the most common PAH to cause cancer in animal and this compound is notable for being the first chemical carcinogen to be discovered. Based on the available evidence both the International Agency for Research on cancer (IARC, 1987) and US EPA (1994) classified a number of PAHs as carcinogenic to animal and some PAH – rich mixture as carcinogenic to human (ATSDR 1993). The EPA has classified seven PAH compound as probable human carcinogens: benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, dibenz(ah)anthracene, and indeno(1,2,3-cd)pyrene.

4. Teratogenicity

Embroyotoxic effect of PAHs have been described in experimental animal exposed to PAH such as benzo (a) anthracene, benzo (a) pyrene and naphthalene. Laboratory studies conducted on mice have demonstrated that ingestion of high level of benzo (a) pyrene during pregnancy resulted in birth defects and decreased body weight in the offspring. It is not known whether these effects can occur in human. However, the center for children's Environmental Health reports studies demonstrate that exposure of PAH pollution during pregnancy is related to adverse birth outcomes including how birth weight, premature delivery, heart inalformations. High prematal exposure to PAH is also associated with lower 1Q at age three, increased behavioural problems at ages of six and eight and childhold asthma cord blood of exposed babies shows DNA damage that has been linked to cancer (DHGSA 1984).

5. Genotoxicity

Genotoxic effects for some PAH been demonstrated both in rodents and in visto tests using mammalian (including human) cell lines. Most of the PAHs are not genotoxic by themselves and they need to be metabolized to the diol exposed which react with DNA, thus inducing genotoxic damage. Genotoxicity plays important role in the carcinogenity process and maybe in some forms of developmental toxicity as well [ATSDR 2010].

Table 3: Summary of the environmental effects of some polycyclic Aromatics Hydrocarbons

PAHs	Effects	Reference
Anthrancene	Toxic, skin sensitizer , eye irritation, nausea, vomiting, diarrhea and confusion.	(ATSDR, 2009)
Acenaphthylene		(ATSDR, 2010)
Benzo(a)anthrance	Toxic , eye irritation.	(Luch , 2005)
Benzo(a)fluoranthene	Toxic, Carcinogenic, heart malformations, childhood asthma, skin irritations.	(Luch , 2005)
Pyrene	Toxic	(ATSDR, 2009)
Benzo(a)pyrene	Toxic , eye irritation	(ATSDR,2009; Cross et al., 2010; Luch, 2005)
Chrysene	Carcinogenic, mutagenic ,birth defects, decrease in body weight, toxic , skin irritants, leukemia, heart malformations, childhood asthma eye irritation, nausea, vomiting, diarrhea and confusion.	(Luch,2005; ATSDR, 2009)
Benzo(k)fluoranthene		
Benzo(j)fluoranthene	Toxic, Carcinogenic , kidney and liver damage and jaundice cataracts.	(Cross et al 2010)
Benzo(b)fluoranthene		(ATSDR, 2010)
Naphthalene	Toxic, Carcinogenic ,Tumors of the gastrointestinal tract and lungs	(Luch , 2005) (ATSDR, 2009)
	Toxic, Tumors of the breast, lungs.	(ATSDR, 2009)
Dibenz(a,h)anthracene	Toxic, Carcinogenic.	
Indeno(1,2,3-cd)pyrene	Toxic, Skin irritants, Breakdown of red blood cell, heart malformations, childhood asthma, eye irritation, nausea, vomiting, diarrhea and confusion.	(ATSDR, 2009)
	Carcinogenic, toxic, cataracts, kidney and liver damage and jaundice cataracts.	
	Carcinogenic, toxic, increase in mammary tumors in rat kidney and liver damage and jaundice cataracts.	

PAH TOXICITY

A wide range of PAH-induced ecotoxicological effects in a divers suite of biota, including microorganisms, terrestrial plants, aquatic biota, amphibians, reptiles, birds and terrestrial mammals have been reported,[Cerniglia, 1992]. Effects have been documented on survival, growth, metabolism and tumor formation, i.e. acute toxicity, developmental and reproductive toxicity, cytotoxicity, genotoxicity and carcinogenicity. However, the primary focus of the toxicological research on PAHs has been on genotoxixity and carcinogenicity.

In these studies, several PAHs have been shown to damage DNA and cause mutations, which in some cases may result in cancer. However, for the unsubstituted PAHs it is not the original compound that reacts with DNA. The PAHs require metabolic activation and conversion to display their genotoxic and carcinogenic properties. This happens as the PAHs are metabolized in higher organisms. PAHs do not accumulate in the same manner as some other lipophilic organic compounds, e.g. PCBs. Instead, they are converted to more water-soluble forms, which facilities their subsequent excretion from the organism [Cerniglia, 1992]. Unfortunately, this may also lead to the formation of reactive intermediates that may react with DNA to form adducts, preventing the gene involved from functioning normally. The DNA-damage may be repaired, but if the repair fails a mutation, i.e. an irreparable genetic damage, will have occurred. Mutation may affect many different functions of a cell, but above all they may induce cancer [Gibson , 1993].

Figure 4, shows the metabolic activation of benzo[a]pyrene . This compound is probably the most thoroughly studied PAH, and is also one of the most carcinogenic compounds known. The initial step in the metabolism of PAHs involves the multifunctional P-450 enzyme system forming different epoxides through the addition of one atom of oxygen across a double bond. The epoxides are short-lived compounds and may rearrange spontaneously to phenols or undergo hydrolysis of dihydrodiols. These products may then be conjugated with glutathione, glucuronic acid or sulfuric acid, to form products that can be excreted by the organism (Kochany et al, 1994). This conjugation process is, thus, regarded as the true detoxification and excretion process. However, the dihydrodiols may also act as a substarate for cytochrome P-450 once again to form new dihydrodiol epoxides e.g. trans-7,8-dihydroxy-7,8-dihydrobenzo[a]pyrene-9,10-oxide,which unfortunately are poor substrates for further hydrolysis. These dihydrodiol epoxides may instead react with proteins, RNA and most seriously, DNA, thus causing mutations and possibly cancer.

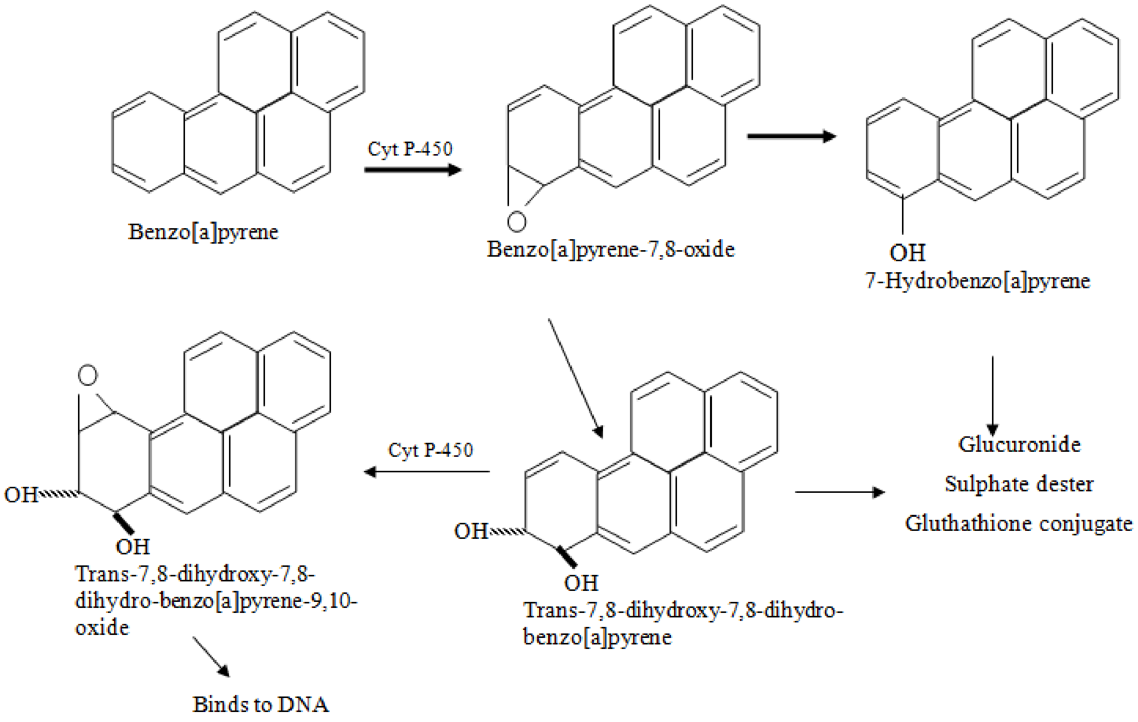

Figure 3. Metabolic activation of Benzo[a]pyrene, from LARC 1983 [25].

ENVIRONMENTAL FATE PROCESSES

PAHs are ubiquitous in the environment, partly because they are transported over long distances without significant degradation (Lunde, et al 1976), e.g., from the United Kingdom and the European continent to Norway and Sweden during winter (Bjørseth, et al 1979). PAHs are sparingly soluble in water and therefore have an affinity for sediment, soil, and biota. When found in air and water, the PAH compounds are generally found adsorbed to particulate matter. Thus, although most PAHs are emitted to the atmosphere, sediments and soils are the major environmental sinks for these compounds. In addition to direct deposition to soils, PAHs can be deposited onto or absorbed by plants, from which they can be washed by rain, oxidized, or be deposited into soil as a result of plant decay (Eisler, 1987). Removal of PAHs from the environment is normally associated with biodegradation or photodegradation processes. The rates of degradation vary and generally decrease with increasing numbers of aromatic rings.

MULTIMEDIA PARTITIONING

With the exception of some of the lighter compounds that volatilize from water or soil, PAHs are relatively non-volatile and of low solubility in water. In the atmosphere, they are mostly found adsorbed to particulate matter that can be removed by wet or dry deposition onto the surface of water bodies, soil, plant surfaces and impervious surfaces. Polycyclic aromatic hydrocarbons released to soil will adsorb to particulate matter where they will be slowly degraded by microbial activity or transported by surface runoff. In aquatic systems, PAHs generally adsorb to suspended matter or sediments, where they tend to persist.

Contamination of groundwater by PAHs can occur as a result of leaching through soils, especially when mobile organic solvents accompany PAHs or when channels are present in the soil (Bedient, et al 1984; Slooff, et al 1989). Naphthalene was the most mobile PAH reported below a creosote-contaminated site in the United States; concentrations of naphthalene at a depth of 3 m were 5% of those at a depth of 0.2 to 0.5 m [Wang, T.H et al 1983]. Contamination of groundwater has been observed following application of oily sludges to soil (PACE. 1988). As in the atmosphere, PAHs in the water column are generally associated with particulates (Harrison, et al 1975; Germain, et al 1988). Volatilization, photolysis, hydrolysis, biodegradation, and adsorption to particulate matter followed by sedimentation are the main processes governing the fate of PAHs in water (NRCC, 1983, Eisler, 1987; Slooff, 1989). The rate of volatilization depends on weather conditions, movement of water, and the molecular weight of the compounds [Slooff, 1989, NRCC, 1983). Polycyclic aromatic hydrocarbons of low molecular weight may volatilize from water, as indicated by the volatilization half-lives of 60 hours naphthalene (Slooff, 1989; Southworth, 1979) and anthracene 17 hours; (Southworth, 1979]. A high molecular weight PAH such as pyrene, however, has a volatilization half-life ranging from 115 hours to 3.2 years (Southworth, 1979). Many of the PAHs in oil spilled on water volatilize (NRCC, 1983). Henry's law constant gives a rough estimate of the equilibrium distribution ratio of concentrations in air and water but cannot predict the rate at which chemicals are transported between water and air. The rates of removal and volatilization of PAHs are strongly dependent on environmental conditions such as the depth and flow rate of water and wind velocity. Although PAHs are released into the environment mainly in air, considerably higher concentrations are found in aqueous samples because of the low vapour pressure and Henry's law constants of PAH. The volatilization half-life for naphthalene from a water body was found experimentally to be 6.3 h, whereas the calculated value was 2.1 h (Klöpffer et al, 1982). Calculations based on a measured air:water partition coefficient for river water 1 m deep with a water velocity of 0.5 m/s and a wind velocity of 1 m/s gave a volatilization half-life of 16 h for naphthalene (Southworth, 1979). The value calculated for evaporative loss of naphthalene from a 1-m water layer at 25°C was of the same order of magnitude (Mackay, et al 1975). Naphthalene was volatilized from soil at a rate of 30% after 48 h, with negligible loss of PAHs with three or more rings (Park, et al 1990).

TRANSFORMATIONS

Ozone-induced oxidation and hydroxylation are the two most important mechanisms by which PAHs are transformed in the atmosphere; both of these reactions are activated by sunlight (Slooff, 1989; NRCC, 1983; Lyman et al., 1982). The photo-oxidation half-lives in air for different PAHs vary from 0.4 to 68.1 hours; photolysis half-lives vary from 0.37 to 25 hours, excluding the long half-life for naphthalene (1704 to 13 200 hours) (Slooff, 1989; USEPA, 1999). These chemical transformations are affected by several factors, including the nature of the particles to which the atmospheric PAHs are adsorbed (NRCC, 1983; Korfmacher, et al 1980; Kamens, et al 1988) and the quantity of PAHs adsorbed to the particulate matter (Slooff, 1989; Kamens et al., 1988). PAHs are more persistent when they are bound to particulates with a high organic carbon content and when present in large quantities on the particulates. Minor transformation pathways for PAHs include reactions with nitrogen oxides (NO_X) and sulphur dioxide ($S0_2$).

DEGRADATION OF PAHS

Degradation of PAHs in the environment occurs through biological, chemical and photochemical processes. These processes may also be utilized for remedial purposes (Kochany et al., 1994). However, the degradation may result in a variety of transformation products some of which could potentially accumulate.

BIOLOGICAL DEGRADATION

Biological degradation appears to be the main process responsible for the removal of PAHs in soil (Wilson et al 1993 ; Sims et al 1983). Microorganisms, such as bacteria and fungi, may transform the PAHs to other organic compounds or to inorganic end products such as carbon dioxide and water (Cerniglia, 1984 ;Gibson ,1993). The latter process has been referred to as mineralization. Some PAH-degrading microorganisms, primarily bacteria, are capable to use the PAHs as a carbon and energy source, and may thus transform the contaminants into molecules that can enter the organisms' central metabolic pathways (Cerniglia, 1984;Cerniglia,1992). Other microorganisms have the capacity to degrade PAHs, while living on a widely available substrate. Such cometabolism does not always result in growth of the microorganism, and sometime the cosubstrate, *i.e.* the PAH, is only transformed into another compound without any apparent benefit for the organism. This may lead to partial degradation, if no enzyme capable of transforming the metabolite is available (Gibson, 1993). For PAHs, the contribution of the cometabolic degradation processes increases as the number of rings in the PAH-molecule increases, since far fewer microorganisms are capable of using the high molecular weight (HMW) PAHs as carbon and energy sources (Cerniglia, 1992;Heitkamp et al 1988;Kanaly et al., 2000).

MICROBIAL DEGRADATION PATHWAYS

PAH-degrading bacteria generally use the PAHs as a carbon and energy source while fungi metabolize the PAHs to more water-soluble compounds, thereby facilitating their subsequent elimination. Bacteria and fungi therefore have different metabolic pathways (Figure 4) (Cerniglia 1984, Cerniglia 1992). The general fungal pathway is quite similar to the transformation pathways found in humans and other mammals. Thus, as can be seen in Figure 2, fungi oxidize PAHs via the cytochrome P-450 enzyme system to form phenols and *trans*-dihydrodiols, which can be conjugated and excreted from the organism. The bacterial degradation of PAHs generally begins with a dioxygenase attack on one of the aromatic rings to form a *cis*-dihydrodiol, which is subsequently dehydrated to catechol (Figure 2). Catechol is a key intermediate from which ring cleavage Degradation of PAHs can occur. The aromatic ring is cleaved between the hydroxyl groups (*ortho* fission) or adjacent to one of the hydroxyl groups (*meta* fission). Successive ring degradation may then occur, so that the structure is ultimately degraded to molecules that can enter the central metabolic pathways of the bacteria (Cerniglia 1984, Cerniglia 1992).

CHEMICAL DEGRADATION OF PAHS

PAHs in soil are also degraded through abiotic processes. Oxidation reactions are the most important in this context, although photochemical reactions may contribute significantly to the degradation on the surface of soils (Kochany et al 1994, Neilson, 1994). In addition, most of the oxidants that commonly initiate the oxidation reactions in the environment, *i.e.* singlet oxygen (1O2), organic peroxides, hydrogen peroxide, ozone and radicals such as alkoxy radicals (RO•), peroxy radicals (RO2•) and hydroxyl radicals (HO•), are directly or indirectly generated through photochemical processes (**Berg et al 1995**). However, some can also be produced from inorganic salts and oxides, especially those of iron and manganese (**Kochany et al 1994**). Chemical oxidation reactions involving hydroxyl radicals, generated from hydrogen peroxide, and ozone, have been most widely studied. Hydroxyl radicals are strong, relatively unspecific oxidants that react with aromatic compounds, such as PAHs, at near diffusion-controlled rates (*i.e.,* kOH*> 109 M-1s-1) (Haag , Yao 1992) by abstracting hydrogen atoms or by addition to double bonds . The ozone molecule may attack double bonds directly, but it can also form reactive hydroxyl radicals by decomposing water (**Gurol** et al 1982). The reaction pathways that follow are very complex, and numerous intermediates are formed. The final reaction products include, for both oxidants, a mixture of ketones, quinones, aldehydes, phenols and carboxylic acids (Kochany et al 1994). Photochemical degradation of PAHs often involves the same oxidative species that are produced during the pure chemical oxidation of PAHs, *i.e.*oxygen, hydroxyl radicals and other radicals. Consequently, the reaction products include similar complex mixtures of ketones, quinones, aldehydes, phenols and carboxylic acids (Kochany et al 1994, Rivas et al 2000)

FATE IN SURFICIAL SOILS

PAHs are adsorbed strongly to the organic fraction of soils and sediments. Some PAHs may be degraded biologically in the aerobic soil layer, but this process is slow because sorption to the organic carbon fraction of the soil reduces the bioavailability. For the same reason, leaching of PAHs from the soil surface layer to groundwater is assumed to be negligible, although detectable concentrations have been reported in groundwater. Polycyclic aromatic hydrocarbons are removed from soils principally by volatilization and microbial activity, the extent of which varies, depending on several factors such as temperature, soil type, presence of other contaminants, and previous contamination [PACE 1988, Wild, 1991]. Low molecular weight PAHs volatilize more rapidly than high molecular weight PAHs [Slooff, W. 1989, Wild, S.R et al 1993]. In a study with sandy loams, forest soil, and roadside soil partially loaded with sewage sludge from a municipal treatment plant, the following half-lives (in days) were found: 14-48 for naphthalene, 44-74 for acenaphthene plus fluorene, 83-193 for phenanthrene, 48-210 for anthracene, 110-184 for fluoranthene, 127-320 for pyrene, 106-313 for benz[a]anthracene plus chrysene, 113-282 for benzo[b]fluoranthene, 143-359 for benzo[k]fluoranthene, 120-258 for benzo[a]pyrene, 365-535 for benzo[g,h,i]perylene, and 603-2030 for coronene (Wild, et al 1993).

BIOTRANSFORMATION

Most living organisms have at least some ability to metabolize xenobiotics. The oxitative metabolism of PAHs in this system proceeds through highly electrophilic intermediate arene oxides, some of which are covalently bound to cellular macromolecules such as DNA, RNA and protein (Miller, 1985). A number of factors exist that primarily determine the availability of organic chemicals to fish for example, while their forms may be greatly modified by physical, chemical and biological events. The changing of the chemical form of contaminants by biological (e.g. biotransformation) or physical means (e.g. photo-oxidation) may greatly alter their availability due to changes in their solubility or reactivity (Oris et al ,1985). PAHs undergoes three types of chemical reactions characteristic of aromatic hydrocarbons (Neff, 1985): electrophilic substitution, oxidation and reduction. Oxidation and reduction reactions destroy the aromatic character of the benzene but electrophilic substitution does not.

The biotrsnsformation of a hydrophobic xenobiotic in fish for example is a major determinants of its toxicity , distributions and ability to be excreted. The biological half-lives of lipophilic xenobiotics would be markedly prolonged without biochemical processes that convert lipophilic compounds to more readly water – soluble and exccretable products.

The major PAHs – metabolization pathways involve cytochrome P450 monoxygenase, expoxide hydrolase and several conjugating enzymes (Fig. 2). These transformation processes are mostly enzymatic and are usually classified into two types:- phase I enzymes (cytochrome P450 monooxygenase system) introduce a polar group into the xenobiotic molecule via oxidative, reductive or hydrolytic processes. Phase II reaction involve the conjugation of xenobiotic or their phase I metabolite, with polar endogenous constituents such as glucuronic acid, sulfate, glutathione or amino acid [Band, et al 2002; Bols, et al 1990] to produce water-soluble conjugates that are easily excreted by fish. The enzymes involved in phase II are called conjugating enzymes.

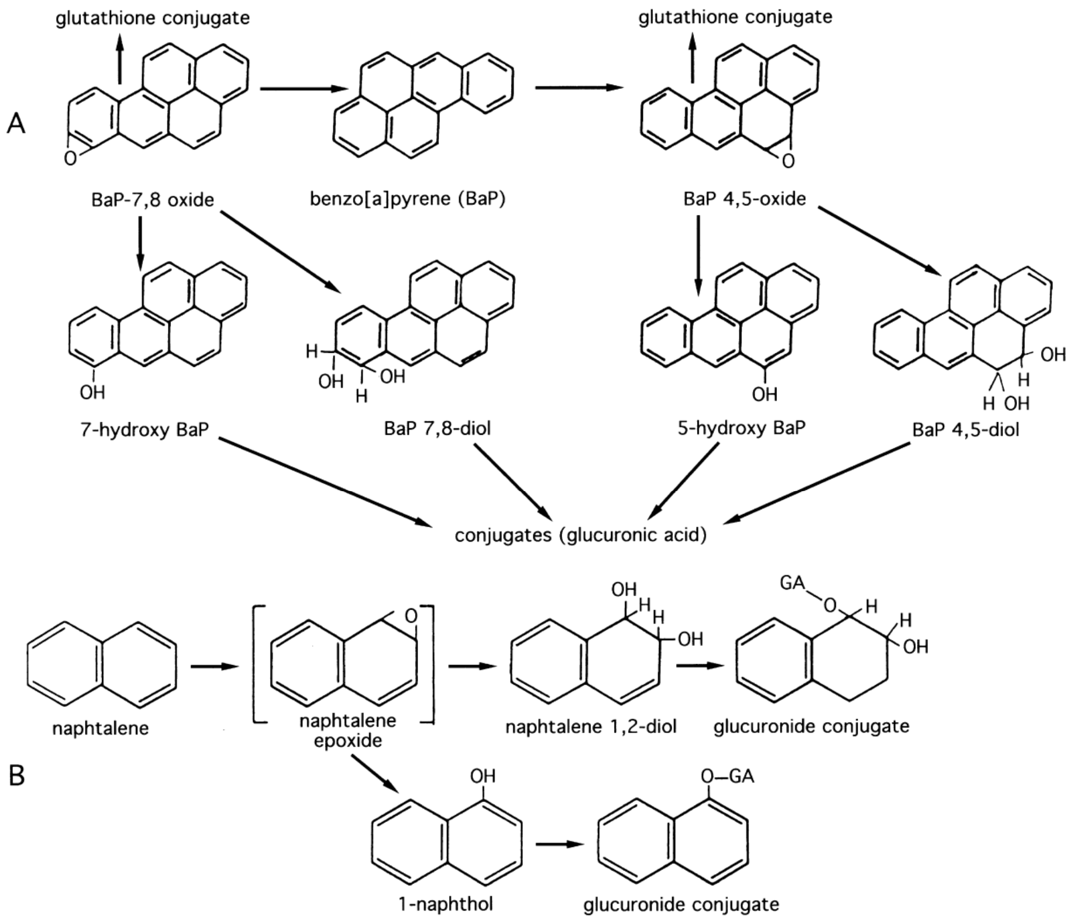

Fig. 2. Biotransformation reactions with representatives of PAHs: A. benzo(a)pyrene (Lee et al. 1972), and B. naphtalene (Khan et al. 1979).

CONCLUSION

Polycyclic aromatic hydrocarbon (PAH) are ubiquitous environmental contaminants. PAHs reveal their toxicity following biotransformation to toxic metabolite which can bound covalently to cellular macromolecules as DNA, RNA and protein. PAHs are released to the environment through natural and synthetic sources with emissions largely to the atmosphere. Natural sources include emissions from volcanoes and forest fires. Synthetic sources provide a much greater release volume than natural sources; the largest single source is the burning of wood in homes. Automobile and truck emissions are also major sources of PAHs. Environmental tobacco smoke, unvented radiant and convective kerosene space heaters, and gas cooking and heating appliances may be significant sources of PAHs in indoor air. PAHs can enter surface water through atmospheric deposition and from discharges of industrial effluents (including wood-treatment plants), municipal waste water, and improper disposal of used motor oil. Several of the PAHs have been detected at hazardous waste sites at elevated levels. In air, PAHs are found sorbed to particulates and as gases. Particle-bound PAHs can be transported long distances and are removed from the atmosphere through precipitation and dry deposition. PAHs are transported from surface waters by volatilization. In soil and sediments, microbial metabolism is the major process for degradation of PAHs PAHs have a potential effect on the environment.

RECOMMENDATION

Five specific PAHs have been judged to be toxic to human health based on long term studies of exposure to PAHs in laboratory animals. The pervasive nature of PAHs and their sources of release present a significant challenge for controlling these compounds. In industry, PAHs are controlled under various laws, regulations and agreements set up to protect the environment and human health.

The sources of PAHs in the home can usually be eliminated or at least controlled to a large degree. Effective methods for keeping the home relatively free of these pollutants are:

- Public education about the sources and health effects of exposure to PAH should be improved.
- Retrofit any open fireplace with an airtight seal.
- Operate wood burning stoves using small, hot fires.
- Ensure wood burning stoves are properly vented and have their own supply of combustion air.
- Install/use a good quality stove top exhaust system.
- Eliminate cigarette smoking indoors.
- The risk of exposure to PAH from passive smoking should be stressed and measures taken to avoid it.
- Ensure that chimneys are properly maintained
- Use a balanced ventilation system to exhaust contaminated air outdoors and replace with fresh air. Recommended ventilation rate is for one-third of the air in the home to be exchanged every hour.
- Owing to their proven immunotoxic effects, coal-tar shampoos should be used for anti-dandruff therapy only if no other treatment is available.
- In view of the proven immunotoxic and carcinogenic effects of PAH in coke-oven workers, exposure to PAH in occupational settings should be eliminated or minimized by reducing emissions to the extent possible or, when they cannot be sufficiently reduced, by providing effective personal protection.
- Use of unvented indoor fires, as in many developing countries, should be discouraged, and they should be replaced by more efficient, well-vented combustion devices.
- Urban air pollution should be monitored all year round and not only seasonally.

This programme also provides suggestions on ways to reduce PAH emissions:

- filtration and scrubbing of industrial emissions,
- treatment of effluents,
- Use of catalytic converters and particle traps on motor vehicles.

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