

LEARNING TOXICOLOGY THROUGH OPEN EDUCATIONAL

POLYCYCLIC AROMATIC HYDROCARBONES (PAHs)

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INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) constitute a large class of organic compounds, environmentally persistent contaminants, with specific structures and varied toxicity, containing two or more fused aromatic rings. Hundreds of individual PAHs are released into the environment from both *anthropogenic processes* (by incomplete combustion or pyrolysis of organic matter) or by *natural processes* (forest fires, volcanic eruptions and biomass biological synthesis and degradation). Since PAHs are detected in air, soil, water and the combustion, pyrolysis and biological processes of organic matter occur everywhere, PAHs are considered ubiquitous in the environment. (Baklanov et al., 2007), (WHO, 2003)

SOURCES OF PAHs

The (PAHs) are formed by pyrogenic, petrogenic, and biological processes.

(a) *Pyrogenic PAHs* are formed when organic matter is exposed to high temperatures (350°C -1200°C) under low oxygen or no oxygen conditions. *Exemples of pyrogenic processes are*: the thermal cracking of petroleum residuals into lighter hydrocarbons, the distillation of coal, the incomplete combustion of fuels in heating systems, of fuels in cars and trucks and of wood in forest fires and fireplaces, etc. Pyrogenic PAHs are generally found in greater concentrations in urban areas and in locations close to *large sources* of PAHs (industrial processes, industrial power generation incineration, etc.) and *smal sources of PAHs* (automotive emissions, smoke from cigarette, wood-burning stoves, jet aircraft exhausts, sewage sludge, etc). (Shafy and Mansour, 2013).The incomplete combustion, either naturally or anthropogenically derived,





has been identified as the single largest contributor of PAHs to the environment (Zhang and Tao, 2009).

(b) Petrogenic PAHs are crude oils formed over millions of years at low temperatures (100–150^oC) and during activities of transportation, storage and use of crude oil/crude oil products, the accumulation of small releases of gasoline, motor oils, and substances associated with transportation, the incomplete combustion of organic substances.

(c) *The natural sources* of PAHs are forest fires, volcanoes, bacterial and algal synthesis, petroleum seeps, and decomposition of biomass. (Shafy and Mansour, 2013; CCME, 2010).

Stationary sources produced about 80% of total annual PAHs emissions; the rest are produced from *mobile sources* (residues from gasoline and diesel-powered vehicle engines, etc). The emissions of PAHs released by industrial production are not important comparing with PAHs produced by incomplete combustion processes, where closed systems and recycling processes are used. New heterocyclic aromatic compounds (carbazole, acridine), as well as derivatives of PAHs, such as nitro-PAHs and oxygenated PAHs can be generated by incomplete combustion and from chemical reactions in ambient air. These compounds occur with PAHs in air, water and food, and the total mixture is referred as polycyclic aromatic compounds PAC. (IARC, 2010).

Some PAHs are used as raw materials:

- Acenaphthene: manufacture of pigments, dyes, plastics, pesticides, pharmaceuticals.
- Anthracene: diluent for wood preservatives and manufacture of dyes and pigments.
- Fluoranthene: manufacture of agrochemicals, dyes and pharmaceuticals. Fluorene: manufacture of pharmaceuticals, pigments, dyes, pesticides and thermoset plastic.
- Phenanthrene: manufacture of resins and pesticides.
- Pyrene: manufacture of pigments.





 Reductions in PAHs emissions occurred since the 1950s, by introduction of the first clean air policies. In present, legislation regarding allowable PAHs concentrations in air, combined with legislation banning the uncontrolled burning of industrial and agricultural wastes, continued to reduce the concentrations of PAHs in ambient air. However, in developing countries (China, India, Brazil, Sudan, etc.) where biomass and coal are the dominant energy sources, PAHs concentrations are still too high. (IARC, 2010; Kim et al., 2013).

CHEMICAL STRUCTURE OF PAHs

The polycyclic aromatic hydrocarbons (PAHs) are a large group of organic compounds comprised of two or more benzene rings bonded in linear, cluster, or angular structures.

Cele mai importante hidrocarburi aromatice policiclice cancerigene sunt prezentate în Tabelul 1. Emisiile de hidrocarburi aromatice policiclice în atmosferă au un tranzit scurt sau lung și se pot acumula în depozite umede sau uscate.

Depending on the number of benzene rings PAHs are classified as: *low molecular weight compounds* consisting of fewer than four aromatic rings and *high molecular weight compounds* of four or more aromatic rings. PAHs with two or three rings (naphthalene, acenaphthene, anthracene, fluorene, phenanthrene) are present in air, predominantly in the vapour phase. PAHs with four rings (fluoranthene, pyrene, chrysene) exist both in the vapour and in the particulate phase, and PAHs having five or more rings benzo[g,h,i]perylene, etc. are found predominantly in the particulate phase. The smaller molecules, such as benzene, toluene and bicyclic aromatic hydrocarbon naphthalene are not considered true PAHs. The most potent PAH carcinogens extensively studied are 7,12-dimethylbenzoanthracene (DMBA) and benzo(a)pyrene (BaP) (CCME, 2010;**Shafy and Mansour**, 2013).





Denumire	Formulă	Denumire	Formulă
(acronim)		(acronim)	
benzo[a]antracen (BaA)		ciclopenta[c,d]piren (CPP)	
benzo[a]piren (BaP)		dibenzo[a,e]piren (DeP)	
benzo[b]fluoranten (BbF)		dibenzo[a,h]antracen (DhA)	
benzo[g,h,i]perilen (BgP)		dibenzo[a,h]piren (DhP)	
benzo[c]fluoren (BcL)		dibenzo[a,i]piren (DiP)	
benzo[j]fluoranten (BjF)		dibenzo[a,l]piren (DIP)	
benzo[k]fluoranten (BkF)		indeno[c,d]piren (IcP)	
crisen (CHR)		5-metilcrisen (5-MC)	CH ₃

Tabelul 1. Exemple de hidrocarburi aromatice policiclice.





From the several hundred chemically related compounds, environmentally persistent, a number of 33 individual PAHs (presented in Table 2) were selected by *The Scientific Committee on Food, based* on their occurrence and toxic effects, as presenting *risks to human health (PAHs in food 2002)*.

Common name	CAS name	CAS	Abbreviation	
		Registry		
		No.		
Acenaphthene	Acenaphthylene	83-32-9 AC	AC	
Acenaphthylene	Acenaphthylene, 1,2-	208-96-8	ACL	
	dihydro			
Anthanthrene	Dibenzo[def,mno]chrysene	191-26-4	ATR	
Anthracene	Anthracene	120-12-7	AN	
Benz[a]anthracene	Benz[a]anthracene	56-55-3	BaA	
Benzo[a]fluorene	11 H-Benzo[a]fluorene	238-84-6	BaFL	
Benzo[b]fluorene	11 H-Benzo[b]fluorene	243-17-4	BbFL	
Benzo[b]fluoranthene	Benz[e]acephenanthrylene	205-99-2	BbFA	
Benzo[ghi]fluoranthene	Benzo[ghi]fluoranthene	203-12-3	BghiF	
Benzo[j]fluoranthene	Benzo[/]fluoranthene	205-82-3	BjFA	
Benzo[k]fluoranthene	Benzo[k]fluoranthene	207-08-9	BkFA	
Benzo[ghi]perylene	Benzo[ghi]perylene	191-24-2	BghiP	
Benzo[c]phenanthrene	Benzo[c]phenanthrene	195-19-7	BcPH	
Benzo[a]pyrene	Benzo[a]pyrene	50-32-8	BaP	
Benzo[e]pyrene	Benzo[e]pyrene	192-97-2	BeP	
Chrysene	Chrysene	218-01-9	CHR	
Coronene	Coronene	191-07-1	COR	
Cyclopenta[cd]pyrene	Cyclopenta[cd]pyrene	27208-37-3	CPP	
Dibenz[a,h]anthracene	Dibenz[a,h]anthracene	53-70-3	DBahA	
Dibenzo[a,e]pyrene	Naphtho[1,2,3,4-	192-65-4	DBaeP	
	<i>def</i>]chrysene			
Dibenzo[a,h]pyrene	Dibenzo[b,def]chrysene	189-64-0	DBahP	
Dibenzo[<i>a,i</i>]pyrene	Benzo[rst]pentaphene	189-55-9	DBaiP	
Dibenzo[<i>a,l</i>]pyrene	Dibenzo[def,p]chrysene	191-30-0	DBalP	
Fluoranthene	Fluoranthene	206-44-0	FA	
Fluorene	9H-Fluorene	86-73-7	3-7 FL	
Indeno[1,2,3-cd]pyrene	Indeno[1,2,3-cd]-pyrene 193-39-5 I		IP	
5-Methylchrysene	Chrysene, 5-methyl- 3697-24-3 5		5-MCH	
1-Methylphenanthrene	Phenanthrene, 1-methyl- 832-69-9 1-M		1-MPH	
Naphthalene	Naphthalene	91-20-3	NA	
Perylene	Perylene	198-55-0	PE	

 Table 2 PAHs presenting risks to human health





Phenanthrene	Phenanthrene	85-01-8	PHE
Pyrene	Pyrene	129-00-0 P	Y
Triphenylene	Triphenylene	217-59-4	TRI
Source: PAHs in food 2002 - Opinion of SCF on the risks to human health			

http://europa.eu.int/comm/food/fs/sc/scf/index_en.html

PHYSICOCHEMICAL PROPERTIES OF PAHS

Pure PAHs are usually colored, crystalline solids at ambient temperature (Masih et al., 2012) The general characteristics of PAHs are high melting and boiling points, low vapor pressure, and very low aqueous solubility. The physical and chemical properties of some selected PAHs are presented in Table 3.

Compound	Melting point (⁰ C)	Boiling point ([°] C)	Vapour pressure (Pa at 25 [°] C)	<i>n</i> Ocyanol: water partitition (Log Kow)	Solubility in water at 25 c ⁰ C (µg/litre)	Henry's law constant at 25 °C (kPa)
Acenaphthylene	92-93	279	8.9 x 10 ⁻¹	4.07	-	1.14 x 10–3
Acenaphthene	95	295	2.9 x 10 ⁻¹	3.92	3.93 x 10 ³	1.48 x 10–2
Fluorene	115–116	340	8.0 x 10 ⁻²	4.18	1.98 x 103	1.01 x 10–2
Phenanthrene	100.5	342	1.6 x 10 ⁻²	4.6	1.29 x 103	3.98 x 10–3
Anthracene	216.4	375	8.0 x 10 ⁻⁴	4.5	73	7.3 x 10–2
Fluoranthene	108.8	393	1.2 x 10 ⁻³	5.22	260	6.5 x 10–4
Pyrene	150.4	400	6.0 x 10 ⁻⁴	5.18	135	1.1 x 10 ⁻³
Benz[a]anthracene	160.7	448	2.8 x 10 ⁻⁵	5.61	14	-
Chrysene	253.8	481	8.4 x 10 ⁻⁵	5.91	2.0	_
Benzo[b]fluoranthene	168.3	480	6.7 x 10 ^{−5}	6.12	1.2 (20 ⁰ C°C)	5.1 x 10 ^{−5}
Benzo[/]fluoranthene	165.4	480	2.0 x 10 ^{−6}	6.12	2.5	-
Benzo[k]fluoranthene	215.7	496	1.3 x 10 ⁻⁸	6.84	0.76	4.4 x 10 ⁻⁵ (20 °C)
Benzo[a]pyrene	178.1	536	7.3 x 10 ⁻⁷	6.50	3.8	3.4 x 10 ⁻⁵
Indeno[1,2,3-	163.6	524	1.3 x 10 ⁻⁸	6.58	62	2.9 x 10 ⁻⁵
<i>c,d</i>]pyrene						(20 °C)
Dibenz[a,h]anthracene	266.6	594	1.3 x 10 ⁻⁸	6.50	0.5 (27°C)	7 x 10 ⁻⁶
Dibenzo[<i>a,i</i>]pyrene	282	525	3.2 x 10 ⁻	7.30	0.17	4.31 x 10 ⁻⁶
Coronene	439		2 x 10 ⁻¹⁰	-	5.4	0.14

 Table 3. Physical and chemical properties of PAHs

Source: Joint WHO 2003





The physicochemical properties of PAHs vary considerable with their molecular weight and structure. The vapor pressure of PAHs decreases with increasing molecular weight and the aqueous solubility decrease with increasing molecular weight. The resistance to oxidation and reduction reactions increase with molecular weight too. PAHs are highly lipophilic and therefore miscible in organic solvents (CMME, 2010). The aqueous solubility decreases for each additional ring added to the PAHs and makes them highly mobile throughout the environment, deposition and revolatilization distributing them between air, soil and water. A specific proportion of PAHs determines their long-range atmospheric transport (LRAT). Once released to the atmosphere, PAHs are found in two separate phases, a vapor phase and a solid phase in which the PAHs are sorbet onto particulate matter. PAHs also present light sensitivity, heat resistance, corrosion resistance and physiological activity (Masih et al., 2012). PAHs possess very characteristic UV absorbance spectra and most PAHs are also fluorescent (Kim et al., 2013). Although the health effects of individual PAHs differ, some PAHs have been identified to be of greatest concern due to highly adverse effects on humans.

PERSISTANCE AND TRANSFORMATION IN OF PAHs IN ENVIRONMENT

PAHs IN ATMOSPHERE

The behavior of PAHs in the atmosphere depends on complex physicochemical reactions, interactions with other pollutants, photochemical transformations, and dry and wet deposition (Zhong and Zhu, 2013). PAHs in the ambient air exist in vapor phase or adsorb into airborne particulate matter depending on the atmospheric conditions (temperature, humidity, origin and properties of the aerosols) and properties of PAHs (Zhang and Tao, 2009). Low-weight PAHs (with two, three, or four rings) exist mainly in the gas phase, are less toxic, but are able to react with other pollutants (ozone, nitrogen





oxides, and sulfur dioxide) to form compounds with high toxicity (diones, nitroand dinitro-PAHs, sulfuric acid. PAHs with four or more rings have insignificant vaporization in environmental conditions and occur mainly in the particulate phase in the atmosphere The concentrations of PAHs in the gas phase increase in summer/in tropical regions, and particulate phase PAHs are dominant during winter in Arctic regions. The adsorption of PAHs onto particulate phases depends on the humidity and on the types of suspended particulates (e.g., soot, dust, fly-ash, metal oxides, pollens, etc.) (Lai et al., 2011; Kim et al., 2013).

PAHs IN SOIL AND WATER

Atmospheric PAHs are continuously deposited to the earth surface by dry or wet deposition processes. PAHs deposited onto the earth's surface can become mobile and will be bound to soil particles, process influenced by the mobility of PAHs particules in the soil, particles size and the pores size of the soil. Studies have found that the octanol-water partitioning coefficient of PAHs is important in determining their sorption to soil. Because the octanol-water partitioning (coefficient (Kow) is related to the solubility of an organic compound in water, as the Kow increases, the aqueous solubility decreases and the tendency of PAHs for sorption to a particular soil increased. The PAHs released to the atmosphere are short- and long-range transported and removed by wet and dry deposition on the soil, water and vegetation. In surface water, PAHs can volatilize, photolyse, biodegrade or bind to suspended particles or sediments. Atmospheric residence time and transport distance depend on the size of particles to which PAHs are adsorbed and on climatic conditions. About 90–95% of particulate PAHs are associated with particle diameters < 3.3 μ m. Particles with a diameter range of $0.1-3.0 \mu m$, with which airborne PAHs are principally associated, present atmospheric residence times of a few days and can undergo ILRT (Shafy and Mansour, 2013; CCME, 2010). Aquatic organisms that metabolize PAHs to little or no extent (algae, molluscs) and the more primitive invertebrates (protozoars, porifers and cnidaria) accumulate high concentrations of PAHs, as would be expected from their log Kow values.





Organisms that metabolize PAHs to a great extent (fish, higher invertebrates), accumulate little or no PAHs. The concentration of PAHs in vegetation is generally lower than that in soil, the bioaccumulation factors ranging from 0.0001 to 0.33 for BaP and from 0.001 to 0.18 for 17 other PAHs tested. Biomagnification of PAHs has not been observed in aquatic systems because most microorganisms have a high biotransformation potential for PAHs. Organisms at higher trophic levels in food chains show the highest potential for biotransformation (WHO 2003; IARC, 2010). Photolysis is the most important factor in the decay of particle-sorbed PAHs in the atmosphere, water and and soil. Half-lives in air are estimated to be in the range of a few minutes to one week, as determined by season (longer in winter), substances and particulate matter composition (WHO, 2003). PAHs in soil can volatilize, undergo abiotic degradation (photolysis and oxidation) biodegrade, accumulate in plants or enter groundwater, and be transported within an aquifer. Based on experimental results, the half-lives (days) of the PAHs in soil were estimated (Table 4)

Compound	Estimated half-lives (days)
Naphthalene	2.1–2.2
Anthracene	10–134
Phenanthrene	16–35
Fluoranthene	268–377
Pyrene	199–260
Chrysene	371–387
Benzo[a]pyrene	229–309

Table 4 The half-lives (days) of the PAHs in soil

Source: WHO, 2003





HUMAN EXPOSURE TO PAHs

Routes of exposure include (a) ingestion food containing PAHs), (b) inhalation polluted ambient and indoor air, smoching or breathing smoke from open fireplaces, (c) dermal contact in both occupational and non-occupational exposure. Tobacco smoke contains a variety of PAHs, such as benzo(a)pyrene, and more than 40 known or suspected human carcinogens. Some crops (wheat, rye, and lentils), may synthesize PAHs or absorb them via water, air, or soil. Water can also contain certain amounts of PAHs because these pollutants can leach from the soil into water or they can enter water from industrial effluents. Soil also contains PAHs, from airborne fallout. Due to the high lipophilicity of PAHs, their presence in organism after ingestion/inhalation is detectable in internal organs rich in adipose tissue. These organs can serve as storage depots from which the PAHs can be gradually released. PAHs entered the organism determine a multistep metabolic activation by specific enzymes from oxidase system, which catalysed the first reaction of epoxidation. HAP epoxides can then be conjugated with glutathione and perform a detoxification reaction. The epoxides that are not conjugated with glutathione are converted into phenols and diols which have to be conjugated with glucuronic or sulfuric acids to enable excretion (WHO, 2003; IARC, 2010; Kim et al., 2013).

OCCURRENCE OF PAH IN FOODS

Raw foods should usually not contain high levels of PAH. In areas remote from urban or industrial activities, levels of PAH found in unprocessed foods reflect the background contamination. Such HAP usually originates from long distance airborne transportation of contaminated particles, as well as natural emissions from volcanoes and forest fires. In the neighborhood of industrial areas or along highways, the contamination of vegetation can be ten-fold higher than in rural areas. Processing of food by drying and smoching, and cooking foods at high temperatures (grilling, roasting, frying) are major sources generating PAH Levels of 130 lg/kg have been found in barbecued meat and 200 lg/kg of PAH





in smoked fish and meat has been reported. Generally, the average background values are in the range of 0.01–1 lg/kg in uncooked foods. The occurrence of PAH in foods is governed by the same physicohemical factors (relative solubility of PAH in water and organic solvents) that determine their absorption and distribution in living organisms. The solubility determines their capacity for transport and distribution between different environmental compartments and their uptake and accumulation by living organisms. The transportation of PAHs in the atmosphere is influenced by their volatility. The chemical reactivity of PAHs influences adsorption to organic material or degradation in the environment. All these factors determine the persistence and capacity of PAH to bio-accumulate in the food chain (PAHs in food, 2002, (CCME, 2010; Shafy and Mansour, 2016)

EFFECT'S ON HUMAN HEALTH

The toxicity of PAHs to aquatic organisms depend on their metabolism and photo-oxidation reactions. PAHs are generally more toxic in the presence of UV radiation and have moderate to high acute toxicity to aquatic life and birds. Mammals can absorb PAHs by various routes (inhalation, dermal contact, ingestion). Plants can absorb PAHs from soils through their roots and translocate them to other plant parts. The uptake rates are generally depending on their concentration, water solubility, and physico-chemical state and soil type. Adverse effects on living organisms include tumors, reproduction, development, and immunity. Data regarding PAHs-induced phytotoxic effects are limited.

Acute (short-term) health effects

The acute impact of PAHs on human health depends on the length /route of exposure, the concentration of PAHs, their relative toxicity and subjective factors (health status and age). The ability of PAHs to induce acute health effects in humans is not clear. The ocupational exposures to high levels of PAHs resulted in eye irritation, nausea, vomiting, diarrhoea and confusion.





Anthracene, benzo(a)pyrene and naphthalene are direct skin irritants and cause an allergic reaction in skin of animals and humans (WHO, 2003; IARC, 2010).

Cronic (long-term) health effects

Cronic (long-term) health impact of PAHs on human health decreased immune system, damage kidney and liver, causes breathing problems, asthma and lung function abnormalities. Repeated contact with skin may induce redness and skin inflammation. Naphthalene can cause the breakdown of red blood cells if inhaled or ingested in large amounts. The harmful effects of PAHs in living organisms that may occur depends on the way of exposure (IARC, 2010, Kim et al., 2013).

Carcinogenicity.

Biological monitoring of exposure to PAHs is of primary interest, due to their toxicity and the widespread diffusion of these compounds in environment. A major concern is the ability of the reactive metabolites (epoxides and dihydrodiols), of some PAHs, to bind to cellular proteins and DNA, leading to mutations, malformations, tumors, and cancer. The long term studies indicate that workers exposed to PAHs have shown an increased risk of skin, lung and gastrointestinal cancers. Benzo(a)pyrene is the first chemical carcinogen discovered and the most common PAH to cause cancer in animals. Based on scientific studies, a number of PAHs are classified as carcinogenic to animals and some PAH-rich mixtures are also classified as carcinogenic to humans (IARC, 2010). The US EPA Agency classified the following seven PAHs compounds: benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, dibenz(ah) anthracene, and indeno(1,2,3-cd) pyrene as probable human carcinogens. (Zhang and Tao, 2009)

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