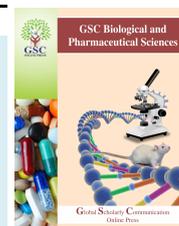


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(REVIEW ARTICLE)



Persistent organic compounds in the environment their impact on human health: A review

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Abstract

Globally the organic contaminants are most widespread persistent organic compounds (POPs). The POPs include polycyclic aromatic hydrocarbons (PAHs), polychlorinated di benzo -p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs), dioxins, antimicrobials, etc. The PAHs are generated by incomplete combustion of coal, diesel, coal tar pitch, tobacco; volcanic eruption and motor vehicle exhaust, etc.; the polychlorinated biphenyls (PCBs), dibenzo-p-dioxins (PCCDs), polychlorinated dibenzofurans (PCDFs) are introduced in the environment via agricultural applications, industrial waste, household wastes. Major exposure routes to the POPs for humans are via inhalation, ingestion, and dermal contact. These contaminants are deposited in marine, freshwater ecosystem and food chain and have adverse effects on organisms and human health. Some of these chemicals have mutagenic and/or carcinogenic properties. In this review methods of the removal of the PAHs have also been discussed.

Keywords: Persistent organic compounds; Polycyclic aromatic hydrocarbons; Environment; Human health; Polychlorinated biphenyls

1. Introduction

Persistent organic compounds one of the most widespread organic contaminants of the environment, are those organic compounds which resist chemical, biological and photolysis degradation in the environment. Polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs), DDT, HCH, chlordane, toxaphene (organic pesticides), antimicrobials and dioxins are stable [1] and toxic to human, animals and aquatic flora and fauna. There are 16 PAHs which are generally found in the environment. Most stabling pesticides in the environment are DDT, HCH, aldrin and dieldrin, chlordane endrin, Chlorpyrifos, mirex, heptachlor; stable mycotoxins are Aflatoxin, ochratoxin, Deoxynivalenol, Zearalenone, Fumonisin; Antimicrobials are tetracyclines, Quinolones, Macrolides, Sulfonamides and PCBs, toxaphene, dioxins and furans [2].

Branded or non-branded toys, mouse pads, bathing shoes, bicycle handles, tools, shoes, sport items, car tyres, synthetic turfs, wood preservatives, road building materials, clay pigeons used for shooting exercise contain persistent organic compounds polycyclic aromatic hydrocarbons [3]. The effects of these pollutants also occur at a far distance from the origin place as these compounds are transported by wind, water. Volatile persistent organic pollutants such as HCH, HCB are dispersed throughout the world even on Polar Regions. As these compounds persist for long periods and are bio accumulated in environment are passed from one species to another via food chain causing harmful effects to the ecosystem and human health. Though many POPs, such as PCBs, DDT, and dioxins are beneficial in pest and disease control, crop production, and industry, these have several adverse effects on human health, and the

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environment. The environmental stability of POPs is because of their lipophilic nature, hydrophobicity, and molecular stability. As PAHs are semi volatile they move in between the atmosphere, and the earth's surface. These compounds are present in all the parts of the environment viz., atmosphere, sea water, groundwater, surface water, soils, air, sewage sludge, and sewage water, plants (crops) even in bovine and mother milk [4-6].

DDT which was used since 1940, for agriculture, forests, home, and for prevention of vector born disease malaria, was banned in the USA and other developed countries since 1972 due to its adverse effects. Maximum consumption of DDT was in the year 1970 and approximately 5.5 lakh ton of DDT were used globally. After 1972 as most of the developed countries banned DDT its use decreased since then. Later on developing countries also banned DDT. At Stockholm in 2001; during the "Convention on Persistent Organic Pollutants" it was inferred to recommend reintroducing DDT in Asian and African countries for controlling the vector-borne disease malaria. So, World Health Organization (WHO) in 2006 reintroduced DDT a hazardous substance in Asia and Africa for controlling the vector-borne disease malaria [7]. Because of which the DDT is still used extensively in China, India and other Asian and African countries [7, 8].

2. Adverse effects of persistent organic compounds

Dermal contact, inhalation, and ingestion are the major routes of the absorption of PAHs and other persistent organic pollutants by mammals. Plants absorb through roots. The human beings inhale PAHs mainly by breathing ambient and indoor air, smoking cigarettes, tobacco smokes. Crops wheat, lentil and rye also contain PAHs either by synthesis or absorption from air, soil, and water ingestion of such crops by the human is another source of PAHs in human beings. Rain or snow causes the return of PAHs containing dust on the earth.

Some short-term effects of PAHs exposure to human is eye irritation, nausea, skin irritation, vomiting, diarrhoea, and confusion [9, 10]. The long-term exposure of PAH to human via any source causes DNA mutations, developmental malformations, leukaemia, decreased immune function, cataracts, oxidative stress, asthma like symptoms, reproductive defects, skin, lung, bladder, bone, brain cancer and scrotal [11-13]. A long prenatal exposure of the high concentration of PAHs is associated with lower IQ [14]. Exposure to DDT may cause neurological and immunodeficiency disorder, brain, pancreatic, breast, prostate cancer [15, 16]. Acetylcholinesterase enzyme activity is also inhibited by DDT [17]. PCBs, PBDEs in the smaller amount can impair the brain development of young ones causing lifelong behavioural impairment. There are also reports of physical and mental development retardation in children who are exposed to POPs. Exposure to PCBs can cause neurological disorder as hyperactivity, reduced memory, attention deficits, and affects immune system. Fish, birds, and mammals in and around the Great Lakes containing POPs show behavioural abnormalities and birth defects. Human whose diets include large amounts of fish, shellfish, or wild foods and sensitive populations with suppressed immune systems are more susceptible to these pollutants.

3. Sources of polycyclic aromatic hydrocarbons (PAH)

The sources of PAHs are natural and anthropogenic activities. The PAHs in the environment enters by three processes,

- (i) Pyrogenic: Pyrogenic PAHs are produced when organic substances been heated at high temperature in absence or low amount of oxygen; destructive distillation of coal; thermal decomposition of petroleum into smaller aromatic hydrocarbons; incomplete combustion of motor fuel; incomplete combustion of fuel oil in the heating system.
- (ii) Petrogenic: Oil spills (oceanic or freshwater), petroleum storage tank leak are some sources of petrogenic PAHs.
- (iii) Biological: Biological PAHs are produced because of degradation of vegetative matter, synthesis by plants and bacteria

3.1. Natural

Forest and bush fires, waste burning, volcanoes, petroleum seeps, decomposition of vegetative litter fall, erosion of petroleum hydrocarbons containing rocks, hydrothermal processes are the natural sources of PAH [18-21].

3.2. Anthropogenic activity

Coal and burning of woods [22], incomplete combustion of oil gas, coal, biomass, garbage, tobacco, charbroiled meat, vehicular exhaust emission, oil exploration (refining), power generation and industrial production, and jet aircraft

exhausts, roofing tar, sewage sludge and creosote materials are some sources because of anthropogenic activities [23-26].

A review of literature denote that globally annually over 6 lakh ton of PAHs are emitted into the atmosphere. China emitted the maximum amount of PAHs followed by India. Wang et al., [27] reported that emission of PAHs in China exceeds 30,000 tons per annum.

4. Reservoirs of POPs

Through effluent runoff, wind air, and atmospheric deposition POPs are deposited in both marine and freshwater ecosystem. POPs are strongly bonded with particulate matter sediments act as reservoirs or sinks of POPs. In the living organisms the POPs are accumulated in the body fat and the concentration magnify on moving from one creature to other. During the monsoon season in India PAHs are transported and deposited to soil, grass, snow, and ice, and sediments [28].

The concentration of PAHs in surface water ranged from 12.78-84.65 ug/L [29, 30]. Karyab et al., [31] found that in the drinking water of Tehran the concentration of the PAHs were 18.8 times higher than the acceptable level as proposed by the WHO and the dermal exposure of PAHs via water sources (swimming and bathing in polluted water) was more than water ingestion. Edokpayi et al., [32] reported that concentration of the PAHs in the river water of South Africa ranges from 15.1-16.6 mg/L; while in wastewater treatment plant it was 13.17 mg /kg. In the river sediments of South Africa the concentration of PAHs ranges from 27.1 to 55.9 mg /kg. These results denote that in the South Africa the Concentration of PAHs were more in sediments samples than water samples. The waste water treatment plants were hot spots for PAHs. They also reported that pyrogenic PAHs were more than petrogenic PAHs.

The concentration of the PAHs in the agricultural soils and sediments globally ranges from 1 mg/kg to 300g/kg based on dry weight [29]. A survey of literature denotes that the concentration of PAHs in the river sediments ranges from 0.3ng g⁻¹ to 0.3 mg g⁻¹. The maximum concentration was reported in the sediment of Haihe River, China [32] while minimum in the sediment of Evrotas River Greece [33]. The PAHs concentration in the sediment of Gomati river (India) ranges from 5.24 to 3722.87 ng g⁻¹ [34], while the PAHs concentration in water ranged from 12.78-84.65 ug/L [29]. Aly Salem et al., [35] during their analysis for PAHs and aliphatic hydrocarbons from the sediments collected from the Suez Gulf, Aqaba Gulf and the Red Sea proper stations Egypt found that total aliphatic hydrocarbon concentration (C₁₄-C₃₂) varied from 33.97 to 553.48 ng/g (mean 174.8 ± 167.06 ng/g), while total PAHs concentrations were between 0.74–456.91 ng/g (mean 32.94 ng/g). In the sediments of Sado estuary the PAHs concentration was up to 7,350 ng g⁻¹ and polychlorinated biphenyls up to 62.2 ng g⁻¹. In the sentinel fish from the Douro River estuary the polychlorinated biphenyls were up to 810.9 ng g⁻¹. The concentration of PAHs in sediments ranged from 0.87-11.23 mg/kg. The accumulation of the PAHs in the soils is due to their strong sorption by soil organic matter and lesser degradation.

Maliszewska-Kordybach et al., [36] reported that PAHs concentration in the Central European agricultural soils ranges from 30 to 4108 ug/ kg while the prevention limit was 1000ug/kg. Kumar et al., [37] during their studies on the concentration of PAHs and related Carcinogenic Potencies in Roadside Soil within a Developing City of Northern India found that the concentration of PAHs in summer, winter, autumn, and the rainy seasons were 16.53, 4.04, 17.49, and 7.82 µg g⁻¹ respectively and the average ratio of a low and high carcinogenic PAHs was found as 1:6, 1:3, 1:7.6, and 1:3.2 respectively. Bortey-Sam et al., [38] studied the concentration of PAHs in the surface soils of Kumasi Metropolis, Ghana and found that total PAHs concentration in the surface soils ranged from 14.78 to 2084 ng/g dry weight (mean 442.5 ng/g). They also reported that Carcinogenic potency of PAHs load was approximately 150 times higher.

Bi et al., [39] during their studies on polycyclic aromatic hydrocarbons in soils from the Central-Himalaya region: Distribution, sources, and risks to humans and wildlife found there is a risk to wildlife and environment of the region because of PAHs beyond permissible limit in the 39% of the soil samples. The concentration of PAHs in soils ranges from 240 to 330 ng/ g dry weight. The additive cancer risk index values (3.8×10^{-3} – 9.2×10^{-1}) indicates the soil PAHs poses a minimum additional risk of cancer to residents via direct contact and using the potable water. They also found that major source (approximately 85%) of PAHs in soils of the Central Himalayas were from pyrogenic origins, out of which 33% was from combustion of coal, 30%, from unburned petroleum hydrocarbons and 22%, from combustion of biomass.

Wang et al., [40] studied the concentration of PAHs in the semi-arid city of Xi'an in Northwest China and found that total concentration in the urban soil ranged from 390.6 to 10,652.8 µg/kg (mean 2052.6 µg/kg), which denote heavy

pollution. The toxic equivalency quantities (TEQs) values ranged in between 21.16 and 1625.78 $\mu\text{g}/\text{kg}$ (mean 423.86 $\mu\text{g}/\text{kg}$) denote a high toxicity potential.

Zhao et al., [41] reported 200 $\mu\text{g}/\text{kg}$ of PAHs in smoked fish meats and 130 $\mu\text{g}/\text{kg}$ in barbecued meat. Mohamed et al., [42] reported that in Egypt, the milk beverages contain 6.07 $\mu\text{g}/\text{g}$ of PAHs, while in milk powder it was 8.2 $\mu\text{g}/\text{g}$, while the concentration of PAHs in the unsmoked cheese and yogurt were 1.3 $\mu\text{g}/\text{g}$.

A review of literature denote that DDT in water ranges from 1 to 5794 ng/L in China, India and other Asian and African countries [43-46], in soil and river sediments it ranges from 0.0086-1600 mg/kg [47]. The total concentrations of the PAHs in sediments ranges from 274.06 $\mu\text{g}/\text{kg}$ to 2656.65 $\mu\text{g}/\text{kg}$, while the total concentrations of the OCPs, PCBs, and PBDEs were 3103.36 $\mu\text{g}/\text{kg}$, 87.31 $\mu\text{g}/\text{kg}$, and 13.88 $\mu\text{g}/\text{kg}$, respectively.

5. Removal of PAHs from environment

PAHs can be removed from the environment by dry deposition, and wet deposition, and hyper accumulation, and by degradation [48, 49].

5.1. Dry deposition

Dry deposition means sorption of PAHs on atmospheric particles settled on the earth [50]. Dry deposition of PAHs depends on sorbent particles, temperature, atmospheric conditions.

5.2. Wet deposition

Wet deposition means precipitation of sorbed contaminants and dissolution of vapour phase PAHs into precipitate [51]. The studies have showed that sorbed contaminants are more removed by this method than vapour phase PAHs [52], the removal of PAHs from air is more removed in summer and spring than in winter.

5.3. Hyper accumulation

Kacalkova and Tlustos [53] during their field studies found that roots of maize (*Zea mays* L.) and sunflower (*Helianthus annuus*) can accumulate 1530 $\mu\text{g}/\text{kg}$ of total PCBs and 3.42 mg/kg of PAHs from the Czech soils. Maize (*Zea mays* L.), sunflower (*Helianthus annuus*), polar (*Populus nigra*) and willow (*Salix x smithiana*) can also accumulate hexa and hepta chlorobiphenyls and their congeners.

5.4. Degradation of PAHs

Degradation of PAHs in the environment occurs via chemical oxidation, biological and photochemical oxidation, leaching, adsorption by soil particles and bioaccumulation.

5.5. Chemical degradation

PAHs undergo three types of the reactions' viz., electrophilic substitution, oxidation and reduction. The aromatic characters of the PAHs are destroyed by oxidation and reduction reactions. PAHs in soils are degraded into a mixture of ketones, aldehydes, phenols, carboxylic acids and Quinone's via oxidation reactions [54]. Oxidation occurs by singlet oxygen, organic peroxides, hydrogen peroxide, alkoxy radicals, peroxy radicals and hydroxyl radicals produced by UV irradiation directly or by oxides of iron and manganese or by photochemical process [55]. Manariotis et al., [56] have reported degradation of PAHs by the high frequency of ultrasound. Qiu et al., [57] during their studies found that PAHs can be removed from the soils by soil washing using sodium dodecyl sulfate (SDS) as the surfactant. Sodium dodecyl sulfate at the concentration of 20 g/L can remove 37-44% of PAHs.

5.5.1. Biological degradation

Microorganisms mainly bacteria (*Gordonia*, *Aeromicrobium*, *Dietzia*, *Mucobacterium*, *Arthrobacter*, *Bacillus*) [58] and fungi degrade aerobically and anaerobically the PAHs into other smaller organic compounds with the end product carbon dioxide, water [59]. Bacterial degradation of the PAHs begins with the formation of cis-dihydrodiol by the attack of dioxygenase on the benzene ring, which in turn are converted into an intermediate catechol from which ring cleavage occurs. Thus, bacteria use the PAHs as carbon and energy source. Fungi convert PAHs into more water-soluble phenolic compounds and trans-dihydrodiols via the cytochrome enzyme P-450.

5.5.2. Photolytic degradation

Photolysis degradation of PAHs occurs when the PAHs excites the electron within the molecule by the absorption of light. Photolysis degradation of PAHs is more effective in vapour phase or in aqueous solution. Low molecular-weight PAHs and linear molecules are most degraded by this process [60].

6. Conclusion

Persistent organic compounds which are natural and anthropogenic contaminants are present in surface water, agricultural soils, and marine sediments, in foods, bovine and mother's milk. Some of POPs are carcinogenic; few are mutagenic to microbes and humans. Daily exposures to POPs are associated with respiratory problems in children and asthma. The maximum emission of PAHs and polychlorinated biphenyls especially of DDT is in the developing countries like China, India. Because of strong bonding in between POPs and particulate matter sediments act as reservoirs or sinks of POPs. The concentration of the PAHs in the agricultural soils and sediments globally ranges from 1 mg/kg to 300g/kg (based on the dry weight). These organic compounds POPs can be degraded by the microbes' algae, bacteria, and fungi. Maize (*Zea mays* L.) and sunflower (*Helianthus annuus*) acts as hyper accumulators for POPs. POPs can also be removed from the environment by dry deposition, and wet deposition, and chemical and photolytic degradation processes.

Compliance with ethical standards

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Disclosure of conflict of interest

None

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