

SOURCES AND BIOACCUMULATION OF TOXIC ORGANIC POLLUTANTS IN THE ENVIRONMENT: A REVIEW ON CURRENT SCENARIO

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ABSTRACT

Persistent organic pollutants (POPs) and other persistent hazardous compounds such as hexachlorocyclohexane (HCH), polyaromatic hydrocarbons (PAHs) and polybrominated diphenylether (PBDEs) have serious health effects due to their toxicity and high tendency to get accumulated in the environment. This paper reviews the prominent sources and distribution of persistent organic pollutants including both natural and anthropogenic sources, responsible for their tenacity in the environment. Their occurrence and abundance in soils, marine sediments, groundwater, aquifers, consumable food items and the atmosphere has been highlighted here. Their persistence in the environment is because of very slow or lack of degradability. POPs can persist for many decades and possibly centuries. Thus it is posing a serious threat to the ecosystems and high risk of contamination of food chains, ground water, drinking water, together with marine ecology. Presence of pesticide residues in the human breast milk, consumable items as well as their bioaccumulation in the water bodies present an alarming situation that needs regular monitoring, assessment and reporting in accordance with appropriate environmental laws, policies and regulations to guarantee health of human and environment. In this paper the sources, world wide occurrence, distribution and toxicity of POPs has been reviewed.

KEYWORDS: Accumulation, Contaminant, Persistent Organic Pollutant, Poly Aromatic Hydrocarbon, Source

INTRODUCTION

All contaminants originated into the environment either by biogenic or anthropogenic sources. But mainly human activities are responsible for their release in huge amounts into the environment. Anthropogenic inorganic and organic pollutants such as polychlorinated biphenyls (PCBs), hexachlorocyclohexane (HCH), polybrominated diphenylether (PBDEs), poly aromatic hydrocarbons, pesticides and heavy metals are dispersed throughout the atmosphere, hydrosphere and lithosphere, and they may get transformed to other compounds which may be even more toxic to flora and fauna (Mansour, 2011). Among these, an anthropogenic persistent organic pollutant (POPs) is an important group of organic toxicants and has been classified as:

- **Pesticides:** Aldrin, Chlordane, dichlorodiphenyltrichloroethane (DDT), Endrin, Heptachlor, Dieldrin, Mirex and Toxaphene;
- **Industrial Chemicals:** polychlorinated biphenyls (PCBs) and HCB and
- **Unintended Industrial by-Products:** Dibenzodioxins and dibenzofurans.

Apart from these a number of chemicals are now recognized as persistent or semi-persistent in the environment and may be included under the Persistent Toxic Substance (PTSs) list. This includes: PAHs (polycyclic aromatic hydrocarbons), phthalate esters, PBDEs (polybrominated diphenyl ethers), PCNs (polychlorinated naphthalenes), BPA (bisphenol A) and alkyl phenols. Persistent Organic Pollutants are consumed by industry, used as pesticides or generated unintentionally as by-products of various industrial/combustion processes. These are widespread in ecosystems

and are the pollutants of great concern due to their potential toxicity, mutagenicity and carcinogenicity. These highly stable compounds can last for years or decades before breaking down. Such types of compounds have higher bioaccumulation and biomagnification potency when they enter into the biotic entities due to their hydrophobicity and very poor water solubility.

Development of technologies, such as bioremediation, biostimulation and bioaugmentation that utilize microorganisms, to detoxify environmental pollutants and transform them into simpler, less toxic compounds is very important in protecting human beings and other organisms from the adverse effects of chemical exposure, and it has become a critical consideration in the regulation of chemicals (Silva et al., 2004; Watanabe et al., 2002). These are known to be endocrine disrupting chemicals having estrogenic, anti-estrogenic or anti-progestin effects. They can even damage the reproductive and immune systems of exposed individuals as well as their offspring. Their adverse effects may lead to death and diseases among humans and animals.

SOURCES OF PERSISTENT ORGANIC POLLUTANTS (POPS) IN THE ENVIRONMENT

Persistent organic pollutants (POPs) are ubiquitous in the natural environment, and originate from two main sources: natural such as biogenic, geochemical and natural fires (Bouwman, 2003) and anthropogenic such as waste burning, fossil fuel combustion, industrialisation, commercial exploitation of the marine environment, agrochemicals, fungicides and pollutants transferred over long distances by marine debris is likely to add the chemical pressure (Ranjan et al., 2012; Bouwman et al., 2012; Sun et al., 2013; Bouwman, 2003; Reindl et al., 2013).

It is the latter source that is the major cause of pollution in the environment. PAHs naturally occur in fossil fuels such as coal and petroleum, but are also formed during the incomplete combustion of organic materials such as diesel, coal, wood and vegetation. Many authors have reported that vehicular activity, wood & coal combustion, pyrolysis, petrogenic source, atmospheric deposition of PAH and surface runoff are the main sources of contamination in the region of Garhwal Himalayas, Sundarban mangrove wetland and Kumaun Himalayan lakes of India (Shukla et al, 2010; Dominguez et al, 2010; Choudhary and Routh et al, 2010).

The other sources leading to contamination in coastal areas include direct discharge of wastes from the densely populated coastal areas, runoff of fertilizers, dumping by vessels, oil spills, deforestation and ill-planned river basin developments (Sarka et al., 2012).

These activities further lead to airborne contamination, which is the main route for pollutants transport over long distances. As in the work reported by Delgado-Saborit et al, 2013, different concentrations of 17 PAH and 15 quinones were measured in air samples collected at a trafficked roadside. And the samples contain four compounds not previously reported in ambient air: 2-methyl-1, 4-naphthoquinone, methyl-1, 4-benzoquinone, 2,6-di-tert-butyl-1, 4-benzoquinone and 2,3-dimethylantraquinone.

Some levels of PCB were also found in air samples collected from some urban areas of Argentina, Brazil, and Chile which were higher than those reported for Falkland Islands (Barra et al., 2006). Further the distribution of PAHs along the roadside studied during winter and autumn season showed their concentration to be more during autumn as compared to winter due to the difference in atmospheric conditions and deposition of PAHs (Kumar et al., 2011).

Another close look at the profiles of pollutants from three sampling sites of Tuscany region, Italy showed the differences that exist between an urban-downtown sites and urban/suburban-background sites. In particular, it was shown that first site is impacted more from vehicles emissions and other sources in its proximities, whereas second site receives

emissions from remote sources only and third is characterized by remote emissions and probably harbours activities (Martellini et al., 2012). Coal, bio-fuel combustion and vehicular exhaust has been characterised as main source of PAHs in the atmosphere of Agra city, too.

Report showed great seasonal variations in the concentration during cold and hot seasons certainly because of change in emission sources and meteorological factors of the city (Rajput and Lakhani, 2010). The major transport pathways for these pollutants were found to be atmospheric deposition and surface runoff (Sarkar et al., 2012). Intake of dust or soils containing some volatile compounds such as HCB, PCB and HCHs (Hong et al., 2013), during feeding to residential birds is likely to be an additional route of exposure to these pollutants.

Point sources that are responsible, originate from petroleum, diesel spills and from industrial processes such as coal liquefaction & gasification during coke production (Dominguez et al., 2010; Sarkar et al., 2012). For example, creosotes and coal tar, which are by-products of coking, contain significant quantities of some pollutants (exp. creosote contains up to 85% PAHs). Deposition of high molecular weight PAHs was also observed in Pichavaram mangrove surface sediments due to some point sources such as lignite and firewood combustion (Ranjan et al., 2012).

Other major sources and direct ingestion into human beings include tobacco smoke and burnt food. The influence of tobacco smoke on levels and phase distribution of PAHs was evaluated by collecting air samples at two homes. The total concentrations of 18 estimated PAHs in home air, influenced by tobacco smoke was 95% higher than at the non-smoking homes, increasing the risk of lung cancer in smoking homes (Castro et al., 2011). In a report on burnt food from Malaysia, Grilled beef satay showed the highest total PAHs among the all forty-two types of meat and fish products widely consumed by Malaysian population.

This indicates higher level of PAHs in grilled meat and fish as compared to other products & it was further proved that internal parts had a significantly lower total PAHs contamination as well as each individual PAH content than exteriors of the same products (Jahurul et al., 2013; Ciecierska and Obiedzinski, 2007). However in a study on charcoal grilled meat samples it was observed that, no carcinogenic PAHs were present after steam and microwave preheating or aluminium wrapping of meat samples (Farhadian, et al., 2011). Thus, these databases can provide useful information in epidemiologic studies to assess health risks associated with dietary PAHs.

Addition to the toxicant levels also occurs by natural processes, such as accidental burning of forests, woodland, and moorland due to lightning strikes. Furthermore, volcanic eruptions and decaying organic matter act as natural sources, contributing to the levels of pollutants in the atmosphere (Manoli and Samara, 1999; Lucchini et al., 2013). PAHs can also have a geochemical origin, as they are formed during pyrolysis which involves the exposure of sediments to high temperatures during sediment diagenesis as observed in Garhwal Himalayas, India and in surface sediments from the coastlines of Guadelope, Spain.

The main source of contamination in sediments was pyrolytic activity (Shukla et al, 2010; Ramdine et al., 2012). PAHs were further analysed in the weathered bottom ash and fresh bottom ash samples obtained from municipal solid waste incinerators. Results showed no difference in the amount of PAHs in the samples, indicating strong bond with the ash and limited release in the surroundings (Johansson and Bavel, 2003).

DISTRIBUTION OF POPS IN SOILS, MARINE SEDIMENTS, GROUNDWATER, AQUIFERS, CONSUMABLE FOOD ITEMS AND THE ATMOSPHERE

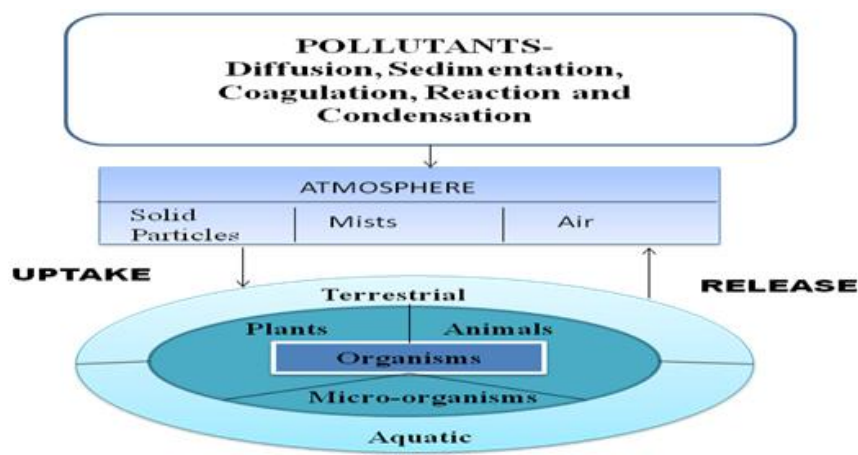


Figure 1: Interchange of Pollutants in Atmosphere, Hydrosphere and Lithosphere

Marine Sediments: The levels of POP have been detected in marine sediments of San Diego Bay, Don Hoi Lot, Thailand (Muangchinda et al., 2013) and the Central Pacific ocean (Ohkouchi et al., 1999). Varied concentration of different pollutants were also measured in water, sediment, aquatic plant, and animal (shrimp and fish) of Nansi Lake (Zhang et al., 2013), and Indian ocean, where industrialisation, commercial exploitation of the marine environment, oil spills, development on the periphery, and pollutants transfer over long distances by marine debris were found to be the main cause of contamination (Bouwman et al., 2012; Sarkar et al., 2012; Barra et al., 2006);

Sewage Sludge Contaminated Soils: Direct input of raw sewage collected from highly urbanised cities into the water resources, increases the concentration of pollutants in the surface sediments of river basins. As the study on residues of 5 classes of persistent organic pollutants (POPs) such as dichlorodiphenyltrichloroethane (DDTs) and its metabolites, polycyclic aromatic hydrocarbon (PAHs) and its congeners, hexachlorocyclohexane (HCHs) and its isomers, indicate its presence in the sediments and the biota (mollusks, fishes and marine mammals) (Leite et al., 2011, Sarkar et al., 2012). Contamination was also observed in the sludge samples collected from wastewater treatment plants of Tunisian. The concentration was highest in the sludge's collected from untreated waste water (Khadhar et al., 2010);

Aquifers, Groundwater and in the Atmosphere: Vehicular exhaust, coal and bio-fuel combustion were characterised as main source of pollutants in the atmosphere. (Rajput and Lakhani, 2010; Jonker and Koelmans, 2002). Many other potential sources of pollution in aquifers includes significant inputs from the river catchment areas, several major sewage outfalls and a series of mud pits that receive contaminated dredged sediments. And different concentrations of thirteen trace elements (Ag, As, Cd, Co, Cr, Cs, Cu, Hg, Mn, Ni, Se, V, and Zn) in the fish tissue (Hung et al., 2004), biomagnification profiles of persistent organic pollutants (POPs) in the aquatic food web of Vietnam (Verhaert et al., 2013; Geyer et al., 2000) and increased POP residue levels in fish tissues directly link its trophic levels and the contaminant accumulation (Corsolini et al., 2007);

Consumable Food Items: Levels of pollutants were measured in crude soya bean oil, olive oil, peanut oil, Fish oil, oil collected from a kitchen range hood, and oil from a fried food stall (Camargo et al., 2012; Wu et al., 2012). Fish oil was identified as one of the most important contributors to the level of Persistent Organic Pollutants (POPs) in feed products (Yebra-Pimentel et al., 2013; Karjalainen et al., 2012), as bioaccumulation of chemicals by aquatic organisms, especially fish, *Daphnia* and mussels, occur because of bio-concentration of the contaminants in marine environments. Furthermore,

persistent organic pollutants (POPs) were found to be transferred from seabirds to coastal food webs (Choy et al., 2010; Van et al., 2002), varied levels of persistent organic pollutants were also present in marine bird eggs, in dairy products, fats, in meat products, edible oils, nuts and in fish (Qin et al., 2011; Sun et al., 2005). High levels of DDT were found in locally produced butter from Kola Peninsula, in pork fat from Arkhangels region and in some fish samples from White Sea and Kargopol region (Bouwman et al., 2012; Polder et al., 2010), PBDE contents were also determined in selected polished food products: butter, pork fat, beef fat, eggs, chocolate and three kinds of fish: salmon and cod (Wojtalewicz et al., 2008). A study on PAHs in coffee brews has also been conducted, showing the influence of roasting and brewing procedures in two Coffee cultivars (Tfouni et al., 2013). However, the difference among the levels detected in different roasting degrees was not statistically significant, except between dark and roasted filtered brews. Similarly for honey and propolis, samples collected from different flowering plants, beekeepers and the local market of Romania, PAHs detected were under detection limit of the method (Dobrinas et al., 2008). It is widely accepted that, for the majority of POPs, the primary route of uptake into the majority of plants is *via* the atmosphere (Currado and Harrad, 2001), and further the terrestrial plants as a vector of human exposure to POPs either directly *-via* consumption of contaminated plant or indirectly *-via* ingestion of meat and dairy produce obtained from animals fed on contaminated plants. A report investigated higher concentrations of PAHs and PAEs on leafy vegetables as compared to gourd and fruit vegetables but it was opposite for OCPs and PCBs (Shen et al., 2013).

Auto Works Site Soils: The concentration of PAHs was much higher in soil samples contaminated from local auto market as compared to the agricultural soil and a number of hydrocarbons degrading bacterial cultures were isolated from contaminated soil sample for further analyses of their degradation efficiency (Bishnoi et al., 2009; Gomare & Lahane, 2011);

Soil: Concentrations of selected POPs have been reported in soil and earthworms collected in grassland, open woodland, in hair and blood of hedgehogs foraging these habitats indicating that earthworms accumulated POPs and that animals feeding on earthworms are potentially exposed to higher concentrations of pollutants (Vermeulen et al., 2010). Soil POPs concentrations and their associated rates of animal and human exposure were highly variable, influenced by multiple factors, and not clearly related to local sources but possibly related to wet atmospheric deposition and the organic carbon content of the soil (Rhind et al., 2013; Barra et al., 2006).

TOXICITY OF POP_S

Many persistent organic pollutants are considered as possible human carcinogens by the International Agency for Research on Cancer (IARC) of the World Health Organization. In addition, to exposure as foetuses in the womb, human beings are exposed to persistent organic pollutants through diet, occupation, and indoor and natural environments (Klopov et al., 1998; Vermeulen et al., 2010). They can cause adverse health effects, such as birth defects, damage to immune and respiratory systems, and critical organs. Specific effects can include cancer, allergies and hypersensitivity, to the central and peripheral nervous systems, reproductive disorders, and disruption of the immune system (Pal et al., 2013). Hormone system dysfunction associated with POPs includes damage to sex-linked disorders. They can also have developmental and carcinogenic effects. Women, infants, and children are especially vulnerable to certain effects of POPs. Evidence suggests that exposure of the foetus to even minute concentrations of some POPs can cause adverse effects in development that persist later in the individual's life (Vermeulen et al., 2010, Mannelje et al., 2013). These effects can include neurophysiological effects, such as attention deficits, learning disorders, behavioral problems. Urban residents are more prone to these effects as compared to the rural ones, due to higher urban-industrial inputs in their environment (Hong et al., 2013; Yu et al., 2013). Presence of organochlorine pollutants, DDTs and PCBs as major contaminants was

also investigated in both abiotic and biotic samples from Lake Como (Italy), Argentina and Chile (Villa et al., 2011; Vieweg et al., 2011). And occurrence of pollutant residues in the human breast milk as well as in the blubber of the endangered gangetic dolphin, indicate that both legacy and new POPs possess a health risk to humans as well as marine mammals (Cullon et al., 2005; Sarkar et al., 2012).

CONCLUSIONS

Thus it can be concluded that, there are a number of sources responsible for amassing of POPs in the environment and their wide distribution in the ecosystems. The major sources that are responsible for their stockpiling include: extensive use of pesticide, fungicides, use of chemicals in food products, oil spills, vehicular exhaust, and coal and bio-fuel combustion. These sources play a vital role in bio-accumulation and distribution of POPs in water bodies, soil and air. Their presence and accumulation in the bio-systems can lead to defects in immune and respiratory systems, birth defects and may even lead to cancer. Therefore, it may be concluded that POPs provide a serious threat to the ecosystems and some strong legislations should be framed and newer robust technologies should be developed to remove the toxicants from environment.

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