

A Review of the Accumulation and Distribution of Persistent Organic Pollutants in the Environment

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Abstract—Persistent Organic Pollutants (POPs) have a long life in soils, sediments, air or biota. There has been a recent upsurge of interest in the development of low cost reliable measures which are required in order to detect and trace current concentration levels of POPs due to increasing levels of accumulation within the living organism. It is accompanied by transformation as well as toxicity makes it ideal to examine the impact on the environment which has been the focus of this review. There are still debates that rage around the issue including relevance of some physiopathologic effects of POPs on the human body along with epidemiological and clinical effects on the human population. Hence in this review there is examination and presenting of arguments in relation to the sources, properties and types of POPs in the atmosphere along with examining the toxicity, analytical techniques and monitoring of atmospheric and biological concentration of POPs in the human population.

Index Terms—Persistent organic pollutants, sources, properties, atmospheric and biological concentration of POP, toxicity.

I. INTRODUCTION

Persistent Organic Pollutants (POPs) are a class of chemical compounds that are derived from a particular series or families of chemicals. POPs have a very long life and they persist in the environment for a long time in soils, sediments, air or biota. There is no consensus among the academic professionals on the exact meaning of the term persistent and how long should a product exist in the environment before they can be labelled as persistent compounds. However, in practice, POPs are classified as compounds which can have half-life period running into many years [1].

Toxicity, high persistence and bioaccumulation ability are factors being focused on in the latest environment based studies. According to the study [2] POPs are among the most important subset of Persistent, Bioaccumulative and Toxic (PBT) chemicals including pesticides like γ -hexachlorocyclohexane or 1,1,1-trichloro-2,2-diethane, polychlorinated biphenyls, polycyclic aromatic hydrocarbons (PAHs), polychlorinated naphthalenes, polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans, as well as groups of brominated flame retardants (BFRs) such as polybrominated biphenyls, hexabromocyclododecane, chlorine-containing molecules like polybrominated diphenyl ethers and tetrabromobisphenol. The overall quantity of POPs in the environment increases due to the massive disposal of PAH and BFR materials, pollution from chemical

plants, combustion of fossil fuels, the wide-spread use of pesticides, and pollution from chemical plants.

The most important challenge to the human society is to reduce the amount of POPs contamination and its spread through the food chain. In order to keep a regular check on the quantity of POPs in food chains, it is necessary to monitor regularly along with the implementation of policies and processes to reduce the amounts of POPs in the food chains. The Stockholm Treaty on POPs [3] was instituted to monitor the concentration levels of POPs in the general population [4]. There are still debates that rage around the issue of social relevance of some physiopathological effects of POPs on the human body along with epidemiological and clinical effects on the human population making it vital to examine, debate and present arguments in relation to the sources, properties and types of POPs in the atmosphere [5]-[9]. The present review presents the toxicity, analytical techniques and monitors the atmosphere in order to know exactly the concentrations of POPs in the human population.

A. Sources of POPs

POPs like dibenzofurans and dioxins are released to the atmosphere by natural sources like volcanic activities or forest fires. POPs as their name suggests, are quite durable and degrade slowly in the environment. Some of the major intentional man-made sources of POPs are industrial sources like incinerating plants, power stations, agricultural sprays, heating stations and evaporation from water surfaces, soil, or from the landfills. Unintentional man made sources of POP are those released from, chemical facilities, wastes containing PCBs (this includes waste that stems from the use of obsolete oil or cooked oil, cement manufacture, lixiviation of dumps, the repairing and maintenance of equipments, sewage sludge, incineration-municipal, hazardous, medical waste, animal carcass incinerator, fly ash storage and combustion of fossil fuels) and diverse combustions [10], [11]. Oceans are identified to be major reservoirs receiving the POPs via numerous rivers and streams and they can be stored as sediments on the bottom of these water bodies and can be released at a later stage

B. Physical Properties of POPs

The chemical and physical properties as well as the type of environment influence the chemical behavior in a particular environment. Physicochemical properties that allow the compound to exist either in the vapor phase or be adsorbed on atmospheric particles are: very low or high lipid solubilities as they decided their bioaccumulation in tissues, high toxicity, and semi-volatility which helps them to travel long distances in the atmosphere before being deposited. Humans are known to store POPs in their fat tissues. Human fat tissues typically store polychlorinated biphenyls (PCBs),

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trans-nonachlor, dioxins, hexachlorobenzene, dichlorodiphenyldichloroethane and the hexachlorocyclohexanes [3]-[15]. However, it has been discovered that humans who eat meat also ingest some of the POPs that occur within the fatty tissues of the animals [16], [17]. Despite banning of most dangerous POPs, there are others such as DDT which is still used widely and is even today being exposed to humans through food chains.

In organic cells, they once again have a tendency to partition into lipids which are then stored inside the fatty tissues of the organisms, rather than entering the aqueous milieu of cells. This is a major reason why POPs tend to accumulate in the food chain as metabolism is a slow process and tends to accumulate in organisms. In the atmosphere, POPs go through slow decomposition in the presence of solar radiation (photolysis), humidity, and other organic and inorganic substances. The heat and other reactive conditions of a particular place determine the persistence of POPs in the atmosphere. While in the tropical regions, many POPs last for only several days, they can last for several years in the polar atmosphere [18]. The consequence of their atmospheric stability is their transport through hundreds and thousands of kilometres. This is the reason behind the transport of pesticides, which are still predominantly used in Africa and South America, to the North Pole region. Confirmation of their transport was done by measuring their presence in ice and snow in the North Pole and also in the organisms present in the North Sea. Since these compounds have never been utilized in the North Pole, their presence shows a confirmation of their transport through long distances [19].

Bioaccumulation leads to bio magnification of some persistent organic substances; hence, these molecules are found to occur at higher concentrations in animals that occupy the highest levels in the food chain. Why this happens is because the predatory animals consume prey hundreds of times their own weight. Many industrial products or by-products are found to consist of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans.

Persistent organic pollutants also have a characteristic in which they tend to turn into a gaseous state under environmental temperatures. Thus they may volatilise from water bodies or the soil or the vegetation into the atmosphere and can travel long distances before they get absorbed or deposited somewhere else. This entire cycle of volatilisation and re-deposition can happen a number of times, as the result that these organic compounds can form at one place and get accumulated at another completely different place. Based on the atmospheric temperature and the physico-chemical characteristics of the chemicals, POPs may exist among particles and aerosols in the atmosphere [19].

C. Types of POPs

1) Pesticides

In many countries, a slow but steady move towards the use of less bioaccumulative or less persistent pesticides has been noticed. However, in countries that are developing, which including the tropical countries, organochlorine pesticides (e.g., HCH, DDT, heptachlor, and chlordane) are still being employed by the farmers and in the control of arthropods of veterinary or medical importance. As a consequence, the

level of HCH and DDT are found to decline in human tissues in developed countries, while their levels are stable in most of developing countries [20].

Pesticides that not bound to soil or accumulated in animals and plants drained into lakes and rivers and then entered the aquatic food chain. Various chlorinated pesticides have been identified in Indonesia, Malaysia, Tanzania, China, Colombia, and Thailand at levels signifying potential severe damage [21]. These pesticides are semi-volatile and hence can be dispersed by air also. According to the study [22], the persistent and semi-volatile compounds, such as HCHs and DDTs, released in the tropics are inclined to be redistributed globally. [23], in a study aiming at the distribution of persistent organochlorine pesticides globally, accounted for high concentrations not only in the countries that are developing, but also in industrialised countries where the use of many compounds has been limited for many years.

The distribution, with respect to latitude, of atmospheric HCHs and DDTs shows that their major source of contamination in global terms has seen a transfer from mid to low latitudes during the 1980s [24], [25]. Weber and Goerke (1996) also discovered that the levels of p,p'-DDE (a metabolite of DDT) have shown an increase in Antarctic fish between the years 1987 and 1991. This reflects that organochlorine pesticides are being used continually and that sometimes it is increasing in countries that are developing and present near the tropics.

2) Polychlorinated biphenyls

Polychlorinated biphenyls (PCB compounds) are reported as environmental pollutants in 1996. Water, sediments, bird tissue, and fish tissue have been contaminated by these PCB compounds. In these compounds, 2–10 chlorine atoms are attached to the biphenyl molecule. The classic example of these compounds is Monochlorinated biphenyls in which a single chlorine atom is attached to the biphenyl molecule. So far, the researchers have identified 209 different PCB carcinogens.

3) Polycyclic aromatic hydrocarbons (PAHs)

As the PAHs are identified to be potential carcinogens, the United States Environmental Protection Agency (EPA) announced 16 PAHs as major pollutants. Following this announcement, there has been more focus on their distribution and adverse effects.

Soil, air and various consumable products are being contaminated with these PAHs. They are present throughout the world as they are emitted by plants after prairie fires. But, anthropogenic processes such as fossil fuel combustion and effluents from industrial processing expel the increased level of PAHs into the environment. PAHs may also be released via agricultural fires and cooking.

II. EVIDENCE FOR LONG-RANGE TRANSPORT OF POPs AND GLOBAL DISTILLATION EFFECT

Global distillation/fractionation effect' is responsible for the prevalence and persistence of POPs in polar regions [26]. The pesticides that have been used in warm climates may evaporate and migrate to cool regions wherein they can be condensed at high levels. This 'rule of the cold wall'

illustrates the prevalence of some organochlorines in circumpolar wildlife [27]. While discussing the migration of DDT from continents to oceans, Goldberg (1975) coined the term 'global distillation'. This effect is also called as the 'cold condensation' (Ottar, 1981), the 'cold finger' [28] or the 'cold trap' [29] effect. It is identified from a recent study that the chronic spatial distribution patterns of organochlorine chemicals has increased in recent years due to the physico-chemical characteristics of these substances and some particular characteristic features of cold environments [26].

As these POPs are volatile and resistant to photolytic, biological and chemical degradation, they become persistent throughout the world. Each continent and even remote areas like the open oceans [24], deserts, the Arctic [30] and the Antarctic (Tanabe *et al.*, 1982; Bidleman *et al.*, 1993) [31], [32] reported high levels of POPs. The distribution of PCBs around the world has been discussed in many studies [33]. Researchers have reported the ubiquitous nature of these chemicals in their studies. It was reported the higher level distribution of POPs in the Polar Regions [26]. Few researchers observed high concentration of some particular organochlorines in seawater, rainfall [34] and wild animals [35]. In a study, HCB concentration in Antarctic fish was found to be the same level as that of North Sea fish [25]. The Arctic marine ecosystems [30] and other ecosystems that include top predators and aboriginal peoples who consume marine mammals and fish in their daily life have been reported with high level of POPs. These ecosystems have been extremely polluted by POPs.

Generally, the distribution pattern of a substance is determined by its volatility and atmospheric temperature. As a result, the highly volatile POPs have a tendency to migrate from hot and temperate areas to colder areas. The migration pattern of POPs to higher latitudes that consists of a sequence of short jumps is called as 'grasshopper effect' in which they stop their migration and take rest at mid-altitudes if there is a change in the seasonal temperature and continue to migrate when there is a favourable temperature [26]. A characteristic environmental condensation temperature or temperature range is possessed by each POP. As these POPs are volatile in nature, they can easily migrate to the Polar Regions by means of air. As a result, based on the degree of volatility they have been distributed throughout the world and this kind of distribution is called as 'global fractionation'. As these pollutants may expel from accumulated chemical reservoirs, they will continue to contaminate the environment even though there is a decline or pause in their release.

III. EXTRACTION OF POPs

Supercritical fluid extraction (SFE) is a extraction technique that makes use of a gas at the critical point wherein the high pressure and temperature make the gas to exhibit fluid like properties in order to extract analytes from the matrix. The main benefit being that the gas extracted can be evaporated without requiring an additional solvent which needs to be removed by further processing. . SFE techniques tend to behave in a different manner in comparison to traditionally used solvent based extraction methods, where

the recoveries can be increased or reduced as per demand. The Pressurized Liquid Extraction (PLE) technique of extraction is an accelerated solvent extraction process was derived from SFE technique. In SFE extractions, certain solvents were included to act as modifiers to mimic classical liquid extractions. Classical extraction recoveries were best matched only by solvent modifiers and SFE without extraction gas and this led to the development of PLE. Another technique used for extraction involved using enclosed vessels in a bid to raise the pressure and subsequently enhance the efficiency of extraction and this technique is called as Microwave assisted extraction (MAE). The heat required for the extraction process is supplied by polar solvents such as water or acetone. San *et al.*, (2005) reported the analysis of samples that were extracted using the MAE process, clearly pointed out that it took far less time to dry out the sample when compared to other processes [36].

Another technique that is used to improve efficiency and decrease the time involved in the analysis process is solid phase extraction. This method also reduces the amount of solvent used for the extraction of water and waste water samples, even with significant particulate loadings [36]. By using this technique the particulates that are gathered by the C18 extraction disks are quantitatively separated without using PLE extraction or Soxhlet. Water sampling in the case of SPMD sampling technique can be done passively using semi permeable membrane devices.

Another study [37] has delved into the passive sampling methods in environmental sampling [34]. The study revealed that passive sampling methods are based up on the unobstructed flow of the analytes from the sampling medium to the collecting medium. The medium lowers the overall requirement for energy significantly along with the cost required for the analysis process due to the fact that reduced sampling events and analyte loss during shipping and storage as the analyte is on a trapping medium.

IV. DOSAGE AND TOXICITY OF POPs

Researchers identified a lot of organic substances that pollute the aquatic environment, particularly they investigated more about the toxic effects of PCBs and (OCs) in aquatic environment. As these organic pollutants are resistant to biological degradation, they have been found in the marine environment for years together. The hormonal disturbances caused by the POPs in humans and their ability to induce abnormal functions of endocrine as well as reproductive systems in humans and animals made POPs a public concern. These pollutants (food and water) are found to create adverse environmental effects and there is no use in having them in this world. These organic pollutants could develop cancer, birth defects, learning disabilities, immunological, behavioral, neurological and reproductive discrepancies in human and other animal species. Furthermore the members of the food chain such as eagles, polar bears, killer whales and human being are also contaminated and through this food chain humans consume a significant amount of POPs, in turn lead to adverse health effects and even death. Their ability to cause endocrine disruption, reproductive and immune dysfunction, neurobehavioral and disorder and cancer have been

demonstrated in various studies.

Exposure to POPs develops reduced immunity, recurrent infections, developmental abnormalities, neurobehavioral impairment and cancer and tumor induction or promotion in infants and children. Few studies proved the ability of POPs to induce breast cancer in human being. These pollutants are prevalent in aquatic environment and the aquatic animals are highly exposed to them. Through food chain, humans consume the pollutants from these aquatic animals and accumulate them in their cells. When compared to adults children are found to be more susceptible to the impacts of contaminants. These contaminants, especially the persistent organic pollutants could easily damage the developing cells of the children [38]. Studies demonstrated the lower intelligent quotient and inability to shut out distractions in the individuals who were exposed to POPs during their childhood.

V. LEVEL OF HUMAN EXPOSURE IN MONITORING OF POPs

The international chemical policy has increasingly given more and more importance to persistent organic pollutants over the years. These pollutants are quite toxic in nature and are of anthropogenic origin that are quite often hard to degrade in nature and also are capable of being transported over long distances through the air. As a result, lindane (γ -HCH) was constrained to six particular uses and technical HCH was limited to use as an intermediate in chemical manufacturing by the POPs protocol which was activated in the year 2003 as part of the UNECE Convention on Long-range Trans boundary Air Pollution's framework. In addition to this, the use of DDT and PCBs were also strictly limited and the use of HCB was completely restricted soon afterwards.

Even a chemical by chemical analysis does not tackle the issue of multiple chemical concentrations along with the POPs. The overall observations of the pollutants may be skewed based on the number of pollutants present with even a specific pollutant in sufficiently large quantities creating combination effects. Two crucial factors for combination effects to occur are the number of chemicals and their concentrations

The government's actions in relation to the use of POPs have to be based on constant monitoring of the amount of POPs in the environment, food chains and in the air [39], [40]. There are two studies that are trying to develop a monitoring system that combines multicompartmental modeling and atmospheric modeling. Tracing the advection of polluted air is another method that can be used by the governments. Trajectory statistics of air mass is clearly given in the guidance on the Global Monitoring Plan for constant organic pollutants of the Stockholm Convention as a tool to support the detection and interpretation of trends of POP concentrations in air [4]. Initially, trajectory statistical methods were used for the evaluation of source attribution related emission and distribution pattern of the traditional air pollutants [41].

VI. CONCLUSION

Today international and national environmental regulatory authorities who have a great deal of interest in protecting the

environment and promoting sustainable activities are encouraged to ensure that they establish chronic as well as dedicated monitoring and research programs which are aimed at assessing the environment for the prevalence of POPs in different environments. The previous studies conducted are mostly long term in nature; there is a need for a research and monitoring strategy similar to those already established from other environments.

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