Spatial and Temporal Trends of POPs in Abiotic Compartments: An Overview

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Introduction

Synthetic organic chemicals that are of high commercial value are evaluated for environmental risk under national and international programs. These chemicals include chlorinated-, brominated-, and fluorinated compounds as well as other compounds that are used in agriculture, industrial and consumer products. Several of them are classified as global persistent organic pollutants (POPs) and are known for their persistent properties, bioaccumulation in the food chain and long-term health effects in aquatic and terrestrial animals including humans [1-4]. The United States Environmental Protection Agency (US EPA)'s High Volume Protection Chemical Challenge (HPV), Canada's Chemical Management Plan (CMP) and other International Programs such as European Union's Registration Evaluation Authorization and Restriction of Chemicals (REACH), United Nations Environment Program (UNEP), all share a common goal of evaluating chemicals of commerce and POPs in the environment. Spatial and temporal trend studies on these synthetic organic chemicals, especially organohalogens have been carried out extensively using environmental (water, soil, sediment), biological samples including fish, human adipose tissues [5-8]. In addition, recent studies on newly emerging contaminants that are leaching from consumer products were attributed to environmental and human exposure leading to harmful biological effects by disrupting endocrine hormone functions.

A recent study by Atina et al. estimated the human cost of long-term low level chemical exposure to endocrine disrupting chemicals costs the United States $340 billion in annual health care spending and lost wages [9]. Representative examples are: Brominated flame retardant exposure (especially PBDEs), leading to IQ points loss and intellectual disability in 43,000 cases with 11 million IQ points loss estimated cost $ 266 billion dollars annually. Exposure to phthalates and low testosterone resulting in increased early mortality (10,700 attributable dealths) estimated cost annually $8.8 billion dollars and multiple exposure with autism and attention deficit/hyperactivity disorder (ADHD) in children (~5,900 cases) estimated annual cost of $2.7 billion [9]. Considering the human cost of chemical exposure, it is necessary to take steps to minimize exposure in a timely way to protect our environment and human health. Considering the physical and biochemical properties of these man-made chemicals, spatial and temporal trend studies are essential for understanding and diminishing their environmental distribution, behavior and to prevent harmful effects on wildlife and humans. This overview addresses the spatial and temporal trends of organohalogen and other emerging contamination in abiotic compartments and future implications of these trends. Existing information was compiled and interpreted to explain the clearance rates in various geographical locations. The conclusions derived are based on temporal trend studies conducted during the past three decades and on the information obtained from the published data.

POPs – Historical Background

The chlorinated, brominated and fluorinated compounds were discovered and put to use during late 1800s and 1900s respectively [Table 1]. Although these chemicals benefitted man-kind, they have led to environmental contamination and have changed the quality of the environment, thus adversely affecting the health of animals and humans worldwide [3]. To protect human health and the environment, the Stockholm Convention was adopted and put into practice by the United Nations Environment Program (UNEP) and listed (in 1995) the following persistent organic chemicals that are needed to be addressed globally: aldrin, chlordane, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex, toxaphene, polychlorinated biphenyls (PCBs), dichlorodiphenyl trichloroethane (DDT), dioxins, polychlorinated dibenzofurans, polycyclic aromatic hydrocarbons, and brominated flame retardants. This list was subsequently (since 2001) expanded and new persistent organic compounds added to the Stockholm Convention List are: chlordecone, α-HCH, β-HCH, γ-HCH (lindane), pentachlorobenzene (PeCB), tetrabromodiphenyl ether (tetra-BDE), perfluorooctanesulfonic acid (PFOS), endosulfans and hexabromocyclododecane (HBCD). Because these compounds were produced and used in varying amounts in different time periods by different countries (Table 1), environmental contamination levels varies in various parts of the world. These compounds are distributed globally via air, water and biological systems. The above mentioned compounds possess properties that make them enable to undergo long-range intercontinental transport via atmosphere, hydrosphere and biosphere.

Table 1. Synthesis, commercial scale production, use and ban/restriction on various persistent organic chemicals in various countries since early 1800s to present. (Compiled from multiple literature).

Synthesis and Commercial Production		**Restriction/Ban**	
Year	**Status**	**Year**	**Status**
1825	PCN Synthesized first time.	1970-80	DDT, Lindane, HCB Ban in many countries.
1833	BHC Synthesized first time.	1980-84	PCN, TBT Regulations Introduced.
1873	DDT Synthesized first time.	1984	DDT Restricted in China.
1881	PCB Synthesized first time.	1990	Toxaphene Ban in the USA.
1910	PCN Production began.	2003	TBT Ban in S. Korea.
1929	PCB Production began.	2005	PBDE Restricted in S. Korea.
1939	DDT Production began.	2009	Remove and Destroy all PCBs in Australia.
1945	HCH (Lindane) Production began.	2010	Reductil (Pharmaceutical) Ban in S. Korea.
1950	Chlordane Introduced.	2013	Phase out HBCD.
1962	*SILENT SPRING*	2015	PFCs & HBCD Restricted in S. Korea.
1962-70	PBDE Production began.	2015	C8 (PFOA) Phase out in consumer products in USA.
		2017	Triclosan Ban in Minnesota (USA).
		2018	Canada Proposes Microbeads Ban.

POPs in Abiotic Compartments- Spatial Distribution

Due to unique properties of POPs, residues were detected in abiotic compartments including air, water, soil, sediment etc. Highly volatile, low molecular weight with high vapor pressure, hydrophobic organic contaminants such as selected congeners of PCBs, metabolites of DDT, hexachlorobenzene, PCNs, PBDEs were distributed globally via long-range atmospheric transport. However, actual concentration in the abiotic compartments varies with geographical location and periods of use. For example, Large quantities of PCBs were manufactured and used predominantly in developed countries such as the USA, Japan, France, Germany, Russia, Italy etc. from 1929 through 1970s. Therefore, relatively higher level of PCB contamination was found in air, water, soil and sediment in these countries than the developing countries that never produced PCBs [3,5]. However, PCBs were transported via atmosphere and deposited in remote regions including Arctic and Antarctic environment and biota [2-5]. PCBs were banned in developed countries during 1970s and 1980s. After banning, the environmental levels of PCBs declined drastically near point source areas [3]. However, the contamination levels of PCBs remain steady and did not show declining trend in open ocean environments for decades [2]. Tanabe estimated that about 143,000 tons of PCBs are present in the terrestrial and coastal air (air, river and lake water, seawater, soil, sediment, biota) and about 231,000 tons of PCBs in Open Ocean (air, seawater, sediment and biota). Land stocked PCBs are about 783,000 tons [10]. On the other hand, DDTs and other chlorinated insecticides were produced in large quantities by both developed and developing countries. Most developed countries banned or severely restricted DDT in 1970s/80s due to bioaccumulation/biomagnification in food chain and declining bird populations due to reproductive and developmental (egg-shell thinning) toxicities. However, many developing countries continue to use DDTs and other organochlorines to combat malaria and other insect borne diseases. Therefore, high concentrations of organochlorine pesticides are still found in Indian waters and sediments. For example, In 1985, Indian government banned the use of pesticides listed in the

Stockholm Convention dirty dozen, with an exception of DDT, which is still used to control malaria [11]. The concentrations of HCHs and DDTs in Kaveri River water (southern India) were found up to 2,300 ng/L and 3,600 ng/L respectively, while sediment, these compounds were reported with maximum concentrations of 158 ng/g d.w. and 9.15 ng/g respectively. Considering, emerging new contaminants such as PBDEs, PFCs, pharmaceuticals, personal care product residues, the contamination levels in river water and waste water samples were comparable to concentrations found in waters from developed nations [1,2].

POPs in Abiotic Compartments- Temporal Trends

Comparison of temporal trend studies in one region with those of another need careful consideration of spatial, chemical and biological factors. The issue of organohalogen pollution is rather complicated since, it is difficult to obtain clear picture of the amount of production and use of these chemicals in various countries. The present review provides a generalized assessment of existing situation for organohalogen trends in the global environment. Figure 1 shows a schematic representation of time perspectives of environmental contamination and potential exposure to wildlife and humans.

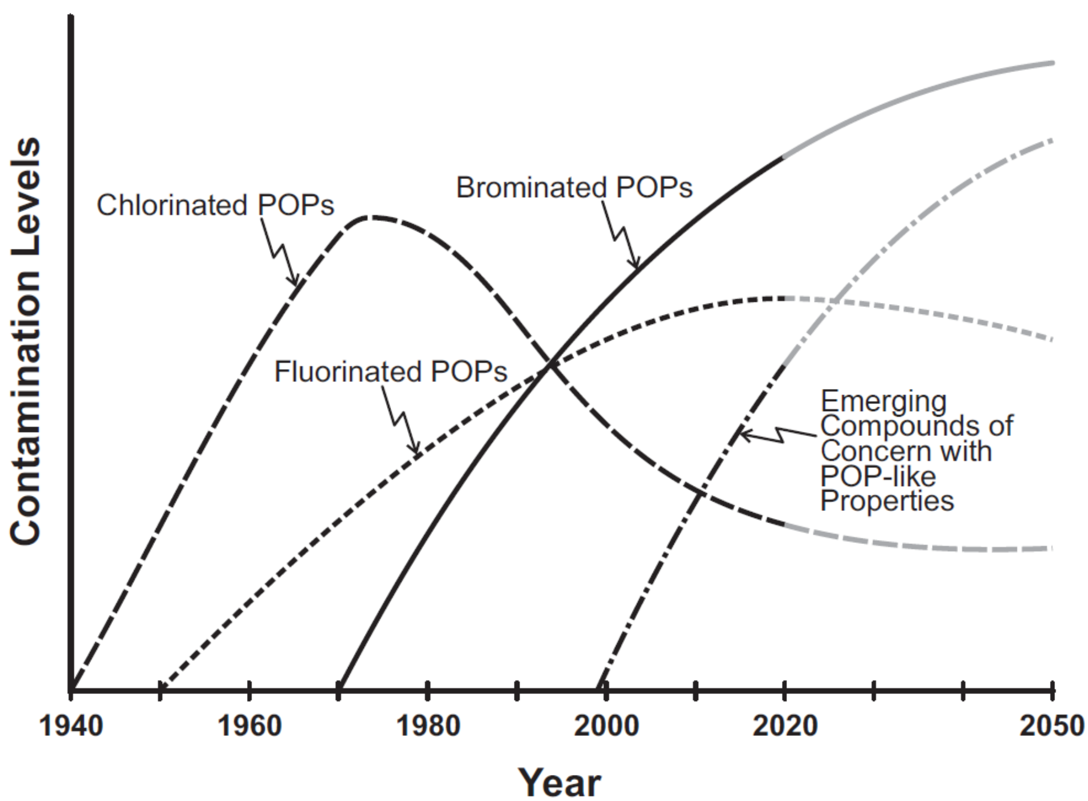

Figure 1. A schematic representation of time perspectives of classical POPs and emerging compounds of concern with POP-like properties. Adapted from reference #2.

Chlorinated compounds such as PCBs and pesticides very rapidly contaminated the environment during the periods of their use for agricultural and public health purposes. The contamination levels declined after the ban/severe restrictions placed on the production and use of these compounds in most of the developed countries. However, developing countries still continue to use these inexpensive chemicals for agricultural pest control and to control insects that spread malaria, typhoid, dengue fever etc. Thus, developing countries form the point source for continued global contamination with the organochlorine compounds. Therefore, future chronic toxic effects in humans and wildlife by organochlorine compounds cannot be ruled out. In contrast, brominated and fluorinated compounds are being produced in large quantities and used globally, both developed and developing countries. These compounds are heavily used in indoors appliances and materials. Human exposure pathway for PBDEs and PFCs are direct and intimate. Considerable data have been amassed on the presence of PBDEs and PFCs in indoor environmental media (air, water, dust, lint, clothing, food packaging materials etc.) and human tissues (blood, breast milk, liver, fetus etc.). Based on PBDEs and PFCs use, their recalcitrant property, bioaccumulation, and biomagnification potential, it can be predicted that the environmental contamination as well as human exposure and health effects by these compounds will continue to increase for several decades in both developed as well as developing countries (Figure 1). These factors need consideration in the effort to minimize exposure to humans from indoor pollution, and dietary exposure to protect human health from possible long-term health effects caused by these organohalogen compounds.

In addition, recent studies have revealed occurrence of several compounds used in flame retardants and alternative compounds introduced to serve as flame retardants, industrial chemicals including perfluorinated compounds, phthalates, bisphenol A and its derivatives, pharmaceuticals and personal care products in various environmental media from both developed and developing countries [2]. Several of these emerging contaminants possess persistent organic pollutant (POP)-like properties. Based on these reports, it may be surmised that the compounds with POP-like properties will be of concern for future environmental contamination and health problems.

References

1. Chakraborty P, Khuman SN, Kumar B, Loganathan BG. (2017). In. *Xenobiotics in Soil Environment: Monitoring, Toxicity and Management. Soil Biology* Vol. **49**. Eds. Hashmi,MS., Kumar,V. and Varma, A. Springer International Publishing. pp. 21-40.
2. Loganathan BG. (2016). In. *Persistent Organic Chemicals in the Environment: Status and trends in the Pacific Basin Countries I*. Eds. Loganathan, BG., Khim, JS., Kodavanti, PR., Masunaga, S. ACS Symposium Series Vol. **1243**. American Chemical Society and Oxford University Press. pp 1-15.
3. Loganathan, BG. and Lam, PKS. (Editors). (2012). Global Contamination Trends of Persistent Organic Chemicals. pp 636. CRC Press, Boca Raton, FL. ISBN: 978-1-4398-3830-3.
4. Kodavanti PR, Loganathan BG, Kurunthachalam SK, Sajwan KS. (2015). *Reference Module in Biomedical Research*. http://dx.doi.org/10.1016/B978-0-12-801238-3.02858-0.
5. Loganathan B, Kannan K. (1994). *Ambio*, **23**, 187-191.
6. Loganathan B, Tanabe S, Goto M, Tatsukawa R. (1989). *Environ. Pollut*., **6,**: 237-251.
7. Loganathan B, Tanabe S, Tanaka H, Watanabe S, Miyazaki N, Amano M, Tatsukawa R. (1990). *Marine Pollut. Bull*., **21**, 435-439.
8. Loganathan BG, Tanabe S, Hidaka Y, Kawano M, Hidaka H, Tatsukawa R. (1993). *Environ. Pollut*., **81**, 31-39.
9. Attina T, Hauser R, Sathyanarayana S, Hunt PA, Bourguignon J-P, Myers JP, DiGangi J. (2016). *Lancet Diabetes Endorcrinol.* http://dx.doi.org/10-1016/S2213-8587(16)30279-0.
10. Tanabe S. (1988). *Environ. Pollut*. **50**, 5-28.
11. Patil NN, Selvaraj KK, Krishnamurthy V. et al. (2015). In. *Water Challenges and Solutions on a Global Scale. ACS Symposium Series Volume* **1206**, Eds. S. Ahuja, et al. American Chemical Society and Oxford University Press. Pp 115-159.

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