Supplementary Reader on Persistent Bio-accumulative and Toxic Chemicals



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Ministry of Environment - Sri Lanka

Project on Environmentally Sound Management and Disposal of PCBs Wastes and PCBs Contaminated Equipment in Sri Lanka

Supplementary Reader on Persistent Bio-accumulative and Toxic Chemicals

Ministry of Environment

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Supplementary Reader on Persistent Bio-accumulative and Toxic Chemicals

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Forward



Chemicals are used in almost all the fields including health, food, education, power and energy, industry, transport, agriculture and apparel sectors as well as in our day-to-day lives for various purposes. According to the United Nations Environment Programme, around 350,000 chemical substances are available in the markets all over the world at present.

Approximately 2.3 billion tons of chemicals are produced annually. This production volume of chemicals is estimated to be doubled by the year 2030 as every year new chemicals enter markets. If appropriate measures are not taken environment pollution can occur due to chemicals infiltrating into the air, water and soil during production, transportation, storage, use and disposal of chemicals.

According to the World Health Organization, humans are exposed to chemicals produced synthetically, to chemicals generated as waste during the production process, and chemicals that exist naturally in the environment and approximately 2 million people die due to exposure to selected chemicals alone every year. At the same time, health issues such as cancers, neurological disorders, kidney diseases, respiratory diseases, diabetes and heart diseases can also be caused when chemicals are not properly managed, while chemical poisoning can be seen to cause various side effects. In addition, it has been observed that chemicals are being misused at times where they are used in committing suicide, which needs to be addressed.

The effects caused to the environment and human health by some of the chemicals are long lasting and complex. For example, effects caused by some organic pollutants such as bioaccumulation, bio magnification and grasshopper effect last long. Some act as endocrine disruptive chemicals (EDC) and studies about such chemicals are still at their initial stages whereas some chemicals are persistent, which stays in the environment for long periods.

Chapter 19 of Agenda 21 of the United Nations has identified “Proper Management of Toxic Chemicals in an Environment-Friendly Manner” as an area that should be focused with priority, taking into account the adverse effects caused to the human health and environment in the use of toxic chemical substances. In addition, special attention has been focused on environment-friendly disposal of chemical substances and waste under Sustainable Consumption and Production, which is the 12th Goal under the Sustainable Development Goals.

The information provided by this book on chemicals will help to enhance the knowledge of students in schools, vocational training institutes and universities. The knowledge will help them to use chemicals safely, protecting themselves and the environment.

Dr Anil Jasinghe
Secretary
Ministry of Environment

Executive Summary

Advances in Chemistry and Chemical Engineering has resulted in the development and synthesis of over a million of new chemicals for application in the areas of CP industry, electronics and communications, pharmaceuticals and healthcare, cosmetics and food. However, some of these chemicals can have severe environmental and health risks which can span across generations. Among these chemicals, persistent organic compounds with bio accumulative and toxic properties can result in irreversible long term environmental impacts and health effects. Raising awareness among parties involved in production, use and disposal of these products is an important step to mitigate the risks. Inclusion of subject matter related to Persistent, Bio accumulative, Toxic Chemicals (PBTs) into school, vocational training and university curricula is one of the most effective ways of realising this goal. It is important in order to benefit from chemicals one has to first understand the chemicals.

The objective of this publication is to provide supporting educational materials related to PBTs by collecting the information available in the scientific literature. The arrangement of subject matter to cater the needs of different levels in education in one publication is a challenging task. The relevant content and the arrangement of chapters were decided through an extensive stakeholder consultation process involving educators at all three levels.

This publication includes blocks of subject contents related to PBTs so that each level of curriculum can be built using these blocks in an appropriate manner. The first chapter gives an introduction that can be used at all levels. The second chapter is on intentional and unintentional sources of PBTs. At school level, a general awareness on unintentional generation of toxic compounds through activities such as open burning of wastes can be included into the curriculum, while at vocational training level, in addition to general awareness on sources of PBTs, knowledge on specific sources related to trainees in targeted occupations can be included. The university curricula can be designed to include a wider coverage depending on the specific discipline.

Chapter 3 provides the information on occurrences of PBTs in the environment while Chapter 4 describes the environmental fate to these materials. Contents on fates of commonly known PBTs can be taught at school and vocational training level, while at university level, the fate of these chemicals can be discussed, in addition to occurrences.

Measurement and Analysis of PBTs given in Chapter 5 is mainly intended for the university curriculum, while the content in Chapter 6 on Control and Management of PBTs can be included in all three levels by adopting given materials to suit individual requirements.

Chapter 7 on Functional Characteristics is mainly for undergraduate and postgraduate programmes in chemical engineering and chemistry disciplines. Topics related to Hazardous Waste Management given in Chapter 8 can be adopted for all three levels and included in this publication based on the recommendations from stakeholders.

The last chapter, which is on Toxicology, targets medical and associated disciplines at university level.

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Introduction

History of Persistent, Bio-accumulative, and Toxic chemicals (PBTs)

The history of chemicals in human life is almost as old as the history of humanity itself. The ancients harnessed the power of the elements to create weapons from ore, salt from the sea and medicine from plants. However, our ancestors did not over-exploit this resource and they knew to live in harmony with the environment. This came to an end with the start of the Industrial Revolution from 1750s to 1840 when humans rejected their hands for machines with key inventions of humanity (McFadden 2018), resulting in an exponential increase of population. This increase in productivity and population caused a greater demand for resources including chemicals to support the increasing numbers and demand generating the material demand consumption societies have generated (Annie Leonard 2007).

Trivia Fact: What was the first metal harnessed by humans?
Copper



People found a new treasure buried under the rocks as a black slimy liquid: crude oil. In the United States, the Drake oil well sparked an oil boom leading to a road from which the human race never turned back. They used crude oil to generate a variety of products including plastics, tar and gas. Due to the advancement in the field of chemistry, mankind learned to synthesize chemicals that meet specific properties needed for applications such as pharmaceuticals, industrial chemicals, agrochemicals, consumer products, and cosmetics. As indicated in the Fig. 1.1, the number of chemicals registered under the Chemical Abstract Service (CAS) reached 159 million in 2020.

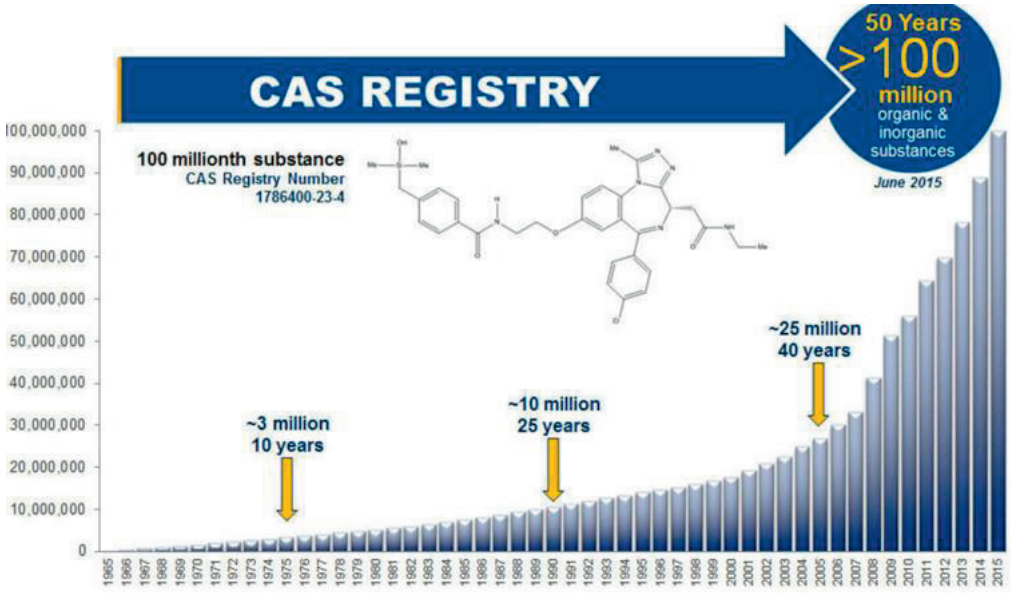


Fig. 1.1 Growth in the CAS REGISTRY over 50 years (Source: Chemical Abstracts Service, 2015)

People realized that the traditional methods of agriculture were insufficient to deal with the new face of mankind. As a consequence, by the third agricultural revolution ("Green revolution") the world gradually moved to intensive agricultural practices that resulted in colossal areas of single-crop cultivation that broke the natural balance of the ecosystem (Vandana Shiva, 2018). Mother Nature responded with her divine wrath of pests and diseases. Humans responded with industrial pesticides including e.g. herbicides and insecticides. The use of chemicals in agriculture and disease control intensified after 1950s. They used chemicals such as DDT (Dichlorodiphenyltrichloroethane) to control epidemics such as malaria and typhus and as a vital insecticide in agriculture. People added toxins such as lead into gasoline and paints, used arsenic as an insecticide, included mercury in paper mills as a slimicide and as a seed dressing to avoid fungal attacks as well as in thermometers and switches (UNEP 2017).

Experience the journey of our use of chemicals with the video links below

https://storyofstuff.org/movies/story-of-stuff/
https://storyofstuff.org/movies/story-of-cosmetics/
https://storyofstuff.org/movies/story-of-electronics/

Thousands of chemicals were developed and entered production and use. Many chemicals were developed as responses to the significant problems at that time, and were found to be extremely effective for solving a certain problem and providing a specific performance. However, the multinational chemical companies, who manufactured these chemicals, were shortsighted as in the case of DDTs or PCBs, because they only looked at a specific need, but not the overall impact of these chemicals on humans or the environment (EEA, 2002). Even during the industrial testing of the developed chemicals, the observations were limited to acute impacts, rather than looking at long term chronic impacts. Industrial manufacturers were extremely delighted with a group of chemicals called chlorofluorocarbons (CFCs) which were extremely stable. They were developed as refrigerants, flowing agents, fire retardants or coolants.

Do you know? : CFCs were so inert to the level that one scientist inhaled the gas in and used it to blow out a candle!

However, the delight was short-lived. Scientists began to notice problems with these chemicals. Rachel Carson wrote her landmark book 'Silent Spring' which cataloged the environmental impacts which coincided with the widespread use of DDT and other pesticides which had been causing harm to wildlife in the United States. Ironically the chemicals which were produced to uplift the standard of living were also found to be carcinogens and/or endocrine disruptors that can interfere with the hormone systems. The high stability of DDT backfired when it was found to be extremely stable up to the level that

resists environmental degradation (persistence). After their use was over, nature could not get rid of them and they existed for very long periods.

The persistent nature of these chemicals also resulted in their accumulation in the animal bodies through food, a term which was coined as bioaccumulation. Carnivores at upper levels in the food chain consumed a lot of herbivores who had these persistent chemicals in their bodies, thus carnivores were at a high risk. The accumulation of chlorinated pesticides in the fatty tissues of animals at the higher trophic levels in the food chain is depicted in Figure 1.2. If you are thinking that the implications are limited to animals, you are sadly mistaken. These persistent chemicals dissolve very well in breast milk, and can pass to newborn infants. In fact, US authorities do not recommend eating some forms of tuna such as swordfish if you are pregnant due to DDT. Not only DDT, but it is also reported that mercury and lead can cause disturbances in our nervous system that can last for a lifetime.

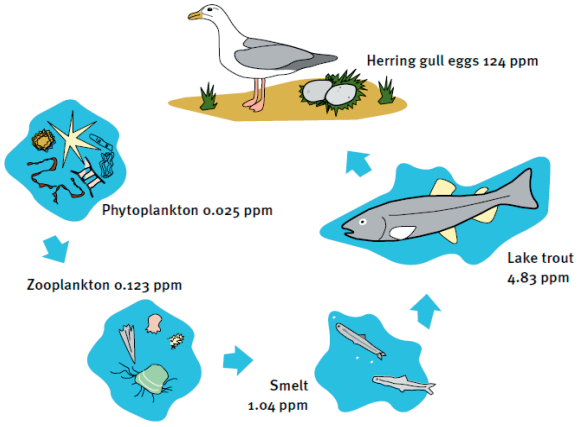


Fig. 1.2 Changes in the concentration of PBTs as they move up the food chain: (Adapted from The North American Mosaic: An Overview of Key Environmental Issues)

These harmful chemicals were coined as PBTs which stood for Persistent, Bioaccumulative and Toxic. Due to the persistence and accumulation in species, these toxicants can spread around the world, even to places where they were never used in the first place. People had to learn from the ill effects of these chemicals from the newspaper headlines.

Do you know? : Animals at the top of the food chain, like polar bears and beluga whales at the North Pole have been detected with fat PCB levels higher than 6 ppm, even though these animals live very far at distances over many latitudes from where these chemicals were used or originated.





Case File 1

In 1965, a young girl was examined by the Chisso chemical factory hospital in Minamata, Japan with rather puzzling symptoms: difficulty in walking, talking and convulsions. Later the girl's sister began exhibiting the same symptoms. Even her neighbour's daughter began showing the symptoms. This led to the authorities discovering a disease that attacked the Central Nervous System. The reason was because of the improper handling and disposal of industrial mercury wastes which caused significant effects to the humans and fauna exposed (Fact sheet-PBTs US EPA; 2010). Mercury was released into the surroundings by the factories into industrial wastewater as methyl mercury and was then bioaccumulated by exposed biota such as shellfish and fish in Minamata Bay and the Shiranui Sea.

After the local public consumed the contaminated seafood it led to a nervous disease, which was named as the Minamata disease. The pollution from the surrounding factories was so great that 2kg of mercury was present in every ton of sediment! The Minamata disaster led the world to realize the potential dangers from environmental pollution and to the characterization of PBTs.


SUNDAY STAR

WEATHER HIGH 30°C | CLOUDY | MAP 58

SUNDAY

STAR INVESTIGATION

A POISONED PEOPLE

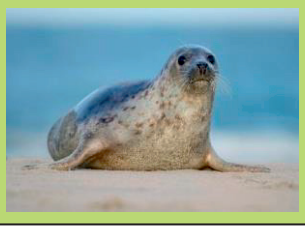
In the decades since mercury destroyed Grassy Narrows' way of life, hundreds have been left sickened, including former chief Steve Fobister. 'My life is gone,' he says

ROAD TO RI

Will I finally a star on Ru

Case File 2

The same disasters were reciprocated in other areas as well. Regardless of DDT being banned 30 years earlier plus years of countless efforts to remedy the region of Puget Sound in Northeastern America from DDT and PCBs, there is still a substantial presence of both compounds which pose a constant risk to human health and the environment (Ulberth; 2000). Harbor seals (*Phoca vitulina*) are a common sight in the Puget Sound area which have been focused to a few studies to monitor and examine the effects of DDT accumulation and magnification in aquatic wildlife. A study marked and re-examined seal pups every 4- 5 years to be tested for DDT concentrations (Ulberth; 2000). The results showed the pups to be highly contaminated; this means their prey was also highly contaminated (Ulberth; 2000).



The problem does not stop with seals. Due to the high lipid solubility of DDTs, it also has the capability to accumulate and aggregate in the tissues of local population who eat seafood from the surrounding areas. This also pressed an issue for pregnant and breast-feeding women, since DDTs will be transported from mother to child. Because of the high economic importance of fishing in the area of Puget Sound stated in the above case file, it will be an important issue to the surrounding human and animal communities.

These headlines caused the world to open their eyes and ears and the world understood the importance of immediate control over persistent, bioaccumulative and toxic (PBT) chemicals to safeguard the environment and human health. Since then, several government agencies have initiated active programs and regulations to restrict the use of these harmful substances. Governments began passing laws that advocates thorough testing and analysis of these chemicals, although that did not become fully effective. A good example is that the US Toxic Substances Control Act (TSCA) which was passed in 1976 and has been basically ineffective in management of chemicals due to weak regulation and ineffective updates. Meanwhile the US Food Quality Protection Act (FQPA) of 1996 was effective to a degree in implementing the pesticide testing requirements.

At the international level, several treaties are in effect to address PBTs and other toxic or harmful chemicals. They include the Stockholm Convention on Persistent Organic Pollutants (POPs), the Minamata Convention on mercury, and the Rotterdam Convention on the Prior Informed Consent (PIC) procedure for certain hazardous chemicals and pesticides in international trade and the Basel Convention to control imports and dumping of hazardous waste into developing countries. Among them, the Stockholm Convention, mediated by the United Nations Environmental Programme (UNEP), mainly focuses on eliminating or reducing the use and release of POPs. It sets up a system for tackling additional chemicals identified as unacceptably hazardous in future situations. Ultimately, the Convention points the way to a future free of dangerous POPs and promises to reshape an economy's reliance on toxic chemicals. (www.pops.int; Toxipedia, POPs;2017).

The objective of this text is to provide information on PBTs including POPs so that they can be used to develop appropriate modules in different undergraduate and postgraduate programs in the Sri Lankan university system.

The first chapter of this text provides a general introduction on PBTs including POPs while chapter 2 focuses on the sources of these chemicals. Chapter 3 is dedicated to describe the occurrence of these chemicals in different environmental matrices and their concentrations. In Chapter 4 of this text, information related to the behavior of these chemicals in the environment comes under the topic “Environmental Fate”. The techniques adopted in sampling and analysis and the precautions that must be practiced during the process are described in Chapter 5.

One of the most important objectives of introducing PBTs related topics to university curricula is creating an intervention to university undergraduates to reduce the exposure and the release of PBTs to the environment in their relevant future fields. These aspects are described in Chapter 6 of the text.

Most of the chemicals falling under the category of PBTs have been synthesized by humans for some specific applications. Understanding the functional characteristics of these chemicals that determines the specific properties in a product is extremely important in finding out alternatives to these chemicals. Chapter 7 titled “Functional characteristics” aims at providing the necessary information on this.

Chapter 8 on “Hazardous waste management” discusses the important aspects related to the management of chemical wastes. Chapter 9 details the toxicological effects of PBT chemicals.

1. General Introduction

1.1 Persistent Bio-accumulative Toxic Substances

Persistent, bio-accumulative toxic substances (PBTs) such as persistent organic pollutants (POPs) such as organochlorine pesticides (OCPs) including DDT, aldrin, dieldrin, and lindane, polyaromatic hydrocarbons (PAHs) such as naphthalene coming from coal, crude oil or gasoline, dioxins, and dioxin-like compounds or heavy metals (e.g. lead, mercury, cadmium) are chemicals that do not degrade readily in the environment. They remain for a very long period in the environment or in the case of heavy metals does not degrade at all. Through food chains, they enter animal bodies. POPs typically accumulate in fatty tissues and are slowly metabolized or broken down in living organisms, often increasing in concentration within the food chain. PBTs have been linked to adverse health effects in both humans and animals, such as mercury, DDT and lead (Gilbert 2008).

PBT impacts on environment and human health due to exposure from food, water, products, soil and house dust including continuous exposure of the entire society at low dose and long term effects is a key factor to be considered in addition to occupational exposure. Hence special attention was drawn towards the PBT/POP chemicals during the 1970-1990 period and the restriction of these substances came into play. Therefore, international conventions were formed to address this issue at a global scale. Such an agreement is the Stockholm Convention (www.POPs.int), signed in 2001 or the Minamata Convention on mercury (http://www.mercuryconvention.org).

1.2 Classification of PBTs

Persistent, Bioaccumulative and Toxic Chemicals have a diversity in chemical species. They can be basically divided into two divisions as inorganic heavy metals which do not contain carbon and Persistent Organic Pollutants (POPs) that contain carbon. The division is explained in Fig. 1.3.

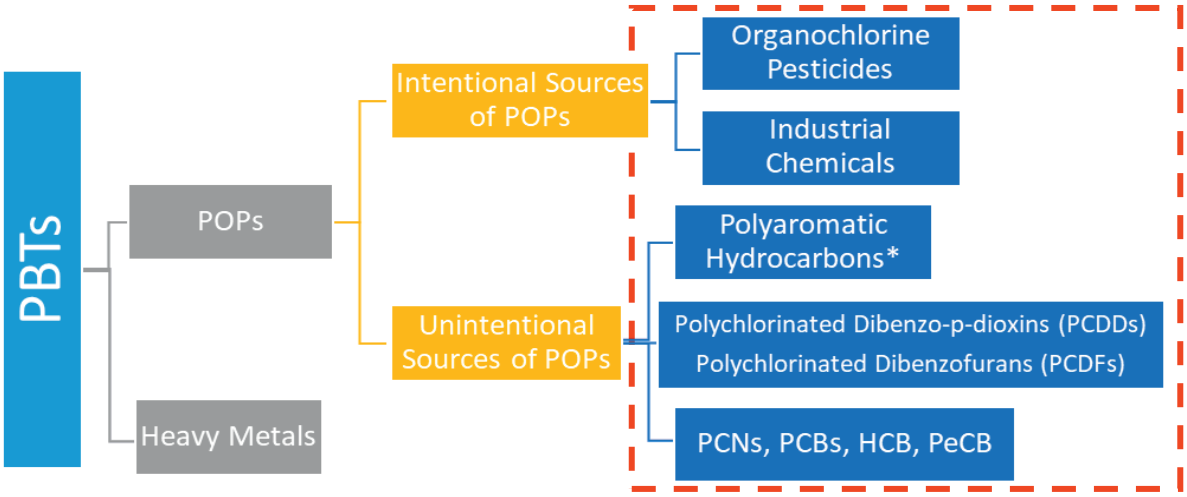


Fig. 1.3 Classification of POPs according to sources

(*PAHs are not listed as POPs in the Stockholm Convention but not in the UNECE protocol)

POPs can be further categorized on the type of source as shown in the Figure 1.3 above. Intentional sources of POPs can be described as instances when the manufacturers produce the specific chemical intentionally with the chemical as the final industrial product. They are released to the environment due to simple use (pesticides or PFOS in firefighting foam) or mishandling and improper disposal e.g.: PCB oils; PFOS in carpets; PBDE in e-waste plastic Several sources produce and release unintentional POPs as an unintended consequence of an intended chemical reaction e.g.: Byproduct in pesticide or pigment production; Emission of polychlorinated dibenzo-p-dioxins (PCDD)/polychlorinated dibenzofurans (PCDF) as from incomplete combustion or secondary metal smelter.

Red dotted rectangular area is the intended scope of study here. Therefore, referring to the above classification three major PBT groups (PBT pesticides, PBT industrial chemicals such as brominated flame retardant or polyfluoroalkyl substances (PFASs) and PBT unintentional byproducts) can be identified and are discussed ahead.

1.2.1 Persistent Organic Pollutants (POPs)

According to the Stockholm Convention, POPs are referred to as organic substances, which dictates that they are carbon-based. They possess a particular combination of physical and chemical properties such that, once released into the environment, they:

- remain intact for exceptionally long periods of time (Persistent),
- become widely distributed throughout the environment as a result of natural processes involving soil, water and, most notably, air,

- accumulate in the fatty tissues of living organisms including humans (bioaccumulation),
- are found at higher concentrations at higher levels in the food chain (biomagnification)
- are toxic to both humans and wildlife (Toxipedia, POPs;2017).

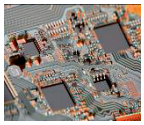
Organochlorine and organobromine POPs molecules show high lipophilicity (accumulation in fatty tissues including human milk). Organofluorine POPs are certain polyfluoroalkyl substances (PFAS) such as perfluorooctanesulfonic acid (PFOS) or perfluorooctanoic acid (PFOA) and related substances which can degrade to PFOS or PFOA. They are water soluble and accumulate in protein rich organs like kidney, brain and blood.

Currently, assessment criterion has identified 28 organic PBTs for control (initial 12 + 16 new) and revived in later chapters. These chemicals fall into three main categories;

1. Pesticides
2. Industrial chemicals
3. Unintended byproducts

All POPs have been divided into the above categories and summarized in Table 1.1

Table 1.1- Classification of POPs according to their functionality stated under Stockholm Convention

PBT chemical	**Functional classification**		
	Pesticides 	Industrial chemicals 	Unintended byproducts 
1. Aldrin	√		
2. Chlordane	√		
3. Chlordecone	√		
4. Decabromodiphenyl ether		√	
5. Dieldrin	√		
6. Endrin	√		

7. Heptachlor	√		
8. Hexabromobiphenyl		√	
9. Hexabromocyclododecane (HBCDD)		√	
10. Hexabromodiphenyl ether and heptabromodiphenyl ether		√	
11. Hexachlorobenzene (HCB)	√	√	√
12. Hexachlorobutadiene (HCBD)		√	√
13. Alpha hexachlorocyclohexane	√		
14. Beta hexachlorocyclohexane	√		
15. Lindane	√		
16. Mirex	√		
17. Pentachlorobenzene	√	√	√
18. Pentachlorophenol and its salts and esters	√		
19. Polychlorinated biphenyls (PCB)		√	√
20. Polychlorinated naphthalenes		√	√
21. Short-chain chlorinated paraffins (SCCPs)		√	
22. Technical endosulfan and its related isomers	√		
23. Tetrabromodiphenyl ether and pentabromodiphenyl ether		√	
24. Toxaphene	√		
25. DDT	√		
26. Perfluorooctane sulfonic acid (PFOS), salts and perfluorooctane sulfonyl fluoride	√	√	

27. Polychlorinated dibenzo-p-dioxins (PCDD)			√
28. Polychlorinated dibenzofurans (PCDF)			√

Although only 22 chemicals are regulated under the Stockholm Convention, studies by Sheringer et al 2012 assessed that rather 570 chemicals can be classified under the parameters of PBTS. Therefore it is likely to assume that the problem is not as narrow as it was expected. This figure was expanded to more than 600 chemicals by Howard and Muir 2010. The OECD (Organisation for Economic Co-operation and Development) has compiled a list of over 4700 per- and polyfluoroalkyl substances (PFAS) and this data has resulted in the Madrid statement which stresses the fact that PFAS production and consumption needs to be limited or replaced with less persistent as non-fluorinated chemicals whenever possible (Blum et al 2017). Therefore the above studies reiterate the fact that we have just analyzed the tip of the iceberg when it comes to the adverse impacts due to PBTS which may be a greater problem than we ever know.

Keep looking forward

Have a look at this video about the need for a toxic free future (Video courtesy of IPEN International POPs Elimination Network)

https://www.youtube.com/watch?v=2sW2pBl9R1A&authuser=0

1.2.2 Heavy Metals

Heavy metals can be defined *as metals or metalloids possessing molecular weights between 63.5 and 200.6 g mol^{-1} and a specific gravity or density greater than 5.0 g cm^{-3}*. There are over 50 elements which can be categorized as heavy metals and 17 of them are considered to be very toxic. (Tchounwou et al 2014)

1.3 Criteria of Determining a PBT

This is a three stage process which includes the following criteria;

- 1st stage- Long-range atmospheric transport potential and toxicity
- 2nd stage- Persistence
- 3rd stage- Bioaccumulation

It is essential to fulfill all three stages, to determine if the substance of concern is a POP or not.

Long-range atmospheric transport potential

Vapor pressure < 1000 Pa

Atmospheric half life > 2 days

Or

Monitoring the evidence in remote regions

And

Toxicity

Potential to adversely affect human and/or the environment

and

Persistence

Evidence that:
½-life in water > 2 months

Or

½-life in soil > 6 months

Or

½-life in sediment > 6 months

Or

Evidence that the substance is otherwise sufficiently persistent to be of concern within the scope of the protocol

and

Bioaccumulation

log K_{ow}- logarithm of the octanol-water partition coefficient

1.4 Definitions of Persistence, Bio-accumulation and Toxicity

1.4.1 Persistence

Some substances are resistant to biological and physical degradation due to their chemical nature. This property is called persistence. It is measured by the half-life of a species in a single environmental medium, e.g. air, water and soil or sediment. The half-life describes the time required for the concentration of a substance to decline to one-half of its original value. This is not entirely an inherent property of the substance but also determined by a combination of substance specific properties and environmental conditions. Therefore, the half-life is dependent on the ecological characteristics, temperature, microbial activity etc. as they may influence the decaying rate. From 1998, persistence criteria became an important part of legally binding national or international frameworks for regulations or international conventions of chemical substances. The EPA (Environmental Protection Agency) has established criteria that categorize a chemical as not persistent, persistent or highly persistent. These criteria are specific to each medium and reflect the half-life of a chemical related to respective media in days.

The PBT profile calculates an atmospheric half-life by determining the prominence of a chemical's reaction with two most prevalent atmospheric oxidants, hydroxyl radicals and ozone. These oxidants play a major role in breaking down chemical compounds into smaller molecules. The half-life is calculated directly from gas phase hydroxyl radical and ozone reaction rate constants. Table 1.2 summarizes the criteria used for determination of persistence of PBT chemicals (Girard, J.E. and Girard, J.; 2014).

Table 1.2- EPA's persistence criteria for PBT chemicals

Media	**Half-Life of Chemical**		
	Not Persistent	Persistent	Highly Persistent
Water	< 2 months	≥ 2 months	> 6 months
Soil	< 2 months	≥ 2 months	> 6 months
Air	≤ 2 days		> 2 days
Sediment	< 2 months	≥ 2 months	> 6 months

The half-life degradation of a chemical in water, soil and sediment is determined by the PBT profiler, a hazard-screening tool capable of predicting the environmental persistence, bio-accumulation potentials, and toxic properties by using survey modules, ultimate biodegradation expert of the BIOWIN, a computerized model used to predict structure related physicochemical, biological, and environmental fates of a chemical compound and the biodegradation rate is indicated in relative terms of hours, hours to days, days, days to weeks and so on. The PBT profiler evaluates the persistence of PBT chemical from a database and issues a report. When viewing the report,

Green font indicates that the chemical is not persistent,

Orange font indicates chemical is persistent

Red font indicates the chemical is highly persistent

For some POPs, in particular perfluoroalkyl substances such as PFOS or PFOA no degradation in ground water or soil is observed. The contamination of precious ground water could lead to pollution for thousands of years and longer.

1.4.2 Bioaccumulation

Some PBTs gradually accumulate in organisms' bodies as these chemicals' rate of discharge from bodies is lesser than rate of entry. This results in much higher concentration of these compounds in animals than in the surrounding environment. This property is termed as biomagnification. For example, concentration of compounds such as dioxin in fish can be thousands of times higher than the concentration in water that they live in.

Green font indicates that the chemical is not expected to bio-accumulate (BCF = 1000),

Orange font indicates the chemical will bio-accumulate (BCF ≥ 1000)

Red font indicates that chemical is highly bio-accumulative (BCF ≥ 5000).

1.4.3 Toxicity

This is evaluated by the PBT profiler considering the potential chronic toxicity of a substance to fish. It estimates the risk by using the Ecological Structure Activity Relationships (ECOSAR) program, which predicts the toxicity associated with chemicals to aquatic organisms such as invertebrates, fish and algae. Structure activity relationships (SARs) are used to predict the aquatic toxicity of chemicals based on the structural similarity to chemicals for which the aquatic toxicity data is already available and express the correlation between compound’s physical or chemical properties and its aquatic toxicity. This helps us to establish

toxicity of chemicals based on structural relationships to an already known toxic substance (Gilbert 2008).

PBT chemicals are known to persist in the environment. They generally occur in low concentrations but can be transported through the biosphere. Other than that, they become bio-concentrated in aquatic organisms and get transported up food chains to humans, wild mammals and birds. Exposure of PBT chemicals generally occurs through the diet and chronic long-term exposure will result in chronic toxicity instead of acute toxicity. The organism may survive in acute effects of such chemicals yet still experience adverse effects from long term exposure in growth or reproduction. Organisms have a lower chance of surviving long-term exposure situations. Therefore, the PBT profiler uses the fish chronic (ChV) estimates from ECOSAR to predict the toxicity, because fish have the potential or likelihood to experience long-term exposure to PBT chemicals. The ChV measures include the acute toxicity of a chemical to fish (fresh water and marine water), water fleas (daphnids) and green algae. The PBT profiler assesses the toxicity of a chemical from a database and issues a report. In report,

Green font indicates that chemical has low toxicity concern (fish ChV > 10 mg/L), or else no effects at all when water is saturated with the chemical,

Orange font indicates a moderate toxicity condition (fish ChV < 10 mg/L)

Red font indicates a high toxicity concern (fish ChV < 0.1 mg/L).

2 Sources

2.1 General Aspects

Persistent Bioaccumulative and Toxic chemicals (PBTs) include Persistent Organic Pollutants (POPs) like polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins and dibenzofurans PCDD/PCDFs; organochlorine pesticides which can persist years or centuries in soils or sediments; and heavy metals like mercury, lead, arsenic, cadmium and chromium which do not degrade at all.

2.2 Sources of Heavy Metals

Heavy metals are released into the environment through natural processes and human-related activities. Volcanic eruptions and natural weathering processes introduce heavy metals into environmental systems. However these amounts are low compared to mining, industrialization and urbanization which make an immense contribution for increasing levels of heavy metals in soils or aquatic environments (Wuana and Okieimen 2011). Industrial effluents are the major source of heavy metals in aquatic ecosystems. Many developing countries including Sri Lanka release industrial effluents and urban runoff into the natural water bodies such as rivers, lakes, streams and oceans without adequate treatment. Human exposure to heavy metals can result in a range of health impacts such as liver and brain damage, cancer, birth defects. Mercury and copper are well known to inhibit the activity of several enzymes in living systems. Some of the industries and the types of heavy metals released from those particular industries are listed in Table 2.1.

Table 2.1: Common heavy metals which are resulted from different industrial effluents. (Tchounwou et al 2014)

Industry	**Metals release to the environment through industrial effluent**
Mining operations and ore processing	As ,Cd, Hg, Mn ,Pb
Metallurgy and electroplating	As, Cd, Cr, Cu, Hg, Pb, Ni, Zn
Chemical industries	As, Cd, Cr, Cu, Fe, Hg, Pb, Zn, Sn
Dyes and pigments	As, Cd, Cu, Fe, Pb
Ink Manufacturing	Fe, Hg, Ni, Co, Cu ,
Pottery and porcelain	As, Cr
Alloys	Sn, Be, Pd
Print	Cr, Pb, Zn
Photography	Ag, Cd, Cr, Mo, Pd

Glass	Co, Pd
Leather tanning	Cd, Cr, Cu, Hg, Zn
Pharmaceuticals	Cr, Cu ,Fe, Hg
Textiles	As, Cd, Cr, Cu, Hg, Pd, Ni
Nuclear technology	Ba, Cd, U
Fertilizer	As, Cd, Co, Cr, Cu, Hg, Pb, Zn
Petroleum refining	As, Cd, Cr, Fe, Hg, Zn

This chapter will focus more on the other categories of PBTs, i.e Persistent Organic Pollutants (POPs) rather than heavy metals.

2.3 Sources of POPs

POPs are released to the environment by human-related activities as well as by natural processes. Volcanic eruptions and forest fires are two probable natural sources of dibenzofurans and dioxins.

However, POPs are known to have a wide range of industrial and commercial applications due to the possession of properties like non-flammability, elevated boiling points, chemical stability and a higher extent of electrical insulation. Furthermore, POPs can be classified into two categories as intentional and unintentional POPs. **Industrial chemicals** and **organochlorine pesticides** are considered as *the main intentional* POPs as these chemicals are intentionally produced for different applications or uses. However, **dioxins, furans and Polycyclic Aromatic Hydrocarbons (PAHs)** are unintentional POPs as they are not produced intentionally, but generate from activities such as combustion and some industrial processes.

2.3.1 Intentional POPs

These are chemicals produced as pesticides or industrial chemicals with intended uses where several of these products were very successful due to their persistence and performance in industrial processes or their toxic potential as pesticides. All listed POPs in the Stockholm Convention are organohalogen compounds containing chlorine or bromine or fluorine as substitutes. These products or their wastes are the sources of intentional POPs in the environment. The compounds containing chlorine are collectively known as organochlorine (OC) compounds. Examples for organochlorines are insecticides like dichlorodiphenyltrichloroethane (DDT) and polychlorinated biphenyls (PCBs). Organobromine chemicals are mainly used as flame retardants in e.g. electronic equipment or polymers in vehicles or construction. Listed POPs are e.g. polybrominated diphenyl ether (PBDEs) or polybrominated biphenyls (PBBs).

This intentional POP sources can be subdivided into industrial chemicals, including chemicals added to consumer products, and organochlorine pesticides as discussed below.

2.3.1.1 Industrial Chemicals

Polychlorinated biphenyls (PCBs)

Polychlorinated biphenyls (PCBs) are found worldwide in sediment, water, bird tissues and fish tissues. Theoretically there are 209 different PCB congeners (similar structures). Most of them are resistant to breakdown and persist in the environment by spreading in atmosphere and water bodies through different transport mechanisms. They also can be transported even to longer distances causing pollution beyond geopolitical borders.

The commercial uses of PCBs include,

- Component of transformers and capacitors
- Electrical equipment including voltage regulators, switches, re-closers, bushings, and electromagnets
- Oil used in motors and hydraulic systems
- Old electrical devices or appliances containing PCB capacitors
- Fluorescent light ballasts
- Cable insulation
- Thermal insulation material including fiberglass, felt, foam and cork
- Adhesives and tapes
- Oil-based paint
- Caulking
- Plastics
- Carbonless copy paper
- Floor finish

Moreover, PCBs can be released to the environment from:

- Poorly maintenance of the sites contaminated with PCBs
- Illegal or improper disposal of PCB wastes
- Leaks or releases from electrical transformers containing PCBs
- Disposal of PCB-containing consumer products into municipal or other landfills which are not designed to handle hazardous waste
- Burning some wastes in municipal and industrial incinerators

2.3.1.2 Organochlorine Pesticides

Pesticides are utilized in controlling pests. They can be classified into three major categories as *insecticides, fungicides and weedicides*. Even though most of these compounds are synthetic man-made chemicals, some naturally occurring plant derivatives were also used in pest control. Approximately, 80% of the pesticides are used in agriculture while non-agricultural applications of pesticides include forestry, landscaping, gardening, food distribution and home pest control.

Do you know? : Nicotine extracts from tobacco leaves were used as an insecticide in the seventeenth century



2.3.2 Unintentionally Formed POPs

Unintentional POPs are produced by the chemical reactions that occur during the combustion of chlorinated compounds. The final pollutant is unknown to the generator or producer as it is generated as an unintended by-product. They are categorized into two categories

1. dioxins
2. furans.

2.3.2.1 Polycyclic Aromatic Hydrocarbons (PAHs)

PAHs consist of two or more fused benzene rings which can be arranged in linear, cluster or angular form. These are ubiquitous (found everywhere) environmental pollutants which are produced as a result of the incomplete combustion of coal, oil, petrol and wood. Natural origins of PAHs in the environment include, open burning, seepage of petroleum or coal deposits and volcanic eruptions. Major human sources of PAHs include fossil fuel burning, by-products of industrial processing, agricultural fires and cooking.

2.3.2.2 Dioxins and Dibenzofurans

PCDD/PCDFs have gained much attention due to their toxic effects since the disastrous chemical accident in Seveso (Italy) in 1976 where a vent of a production vessel of 2,4,5-trichlorophenol collapsed and released a highly toxic cloud including 2,3,7,8-TCDD into the Italian environment (https://en.wikipedia.org/wiki/Seveso_disaster; https://www.youtube.com/watch?v=MRLvxElej6s). The production and use of organochlorine pesticides like the pesticides pentachlorophenol, 2,4,5-T, 2,4-D and PCBs were contaminated with PCDD/PCDFs and their use since 1930s (PCP, PCB) and since the 1940s (e.g. 2,4,5-T, 2,4-D, chloronitrophene, PCNB) where highly contaminated with PCDD/PCDFs until the 1980s and have contaminated the global environment (for Japan see the Figure 2.1).

Furthermore, PCDD/PCDFs are formed and released in waste incinerators and metal industries or open waste burning which are major sources today. Due to their high persistence the contamination of the releases of the last 120 years of chlorine and organochlorine industry and thermal sources remain partly in soils and sediments.

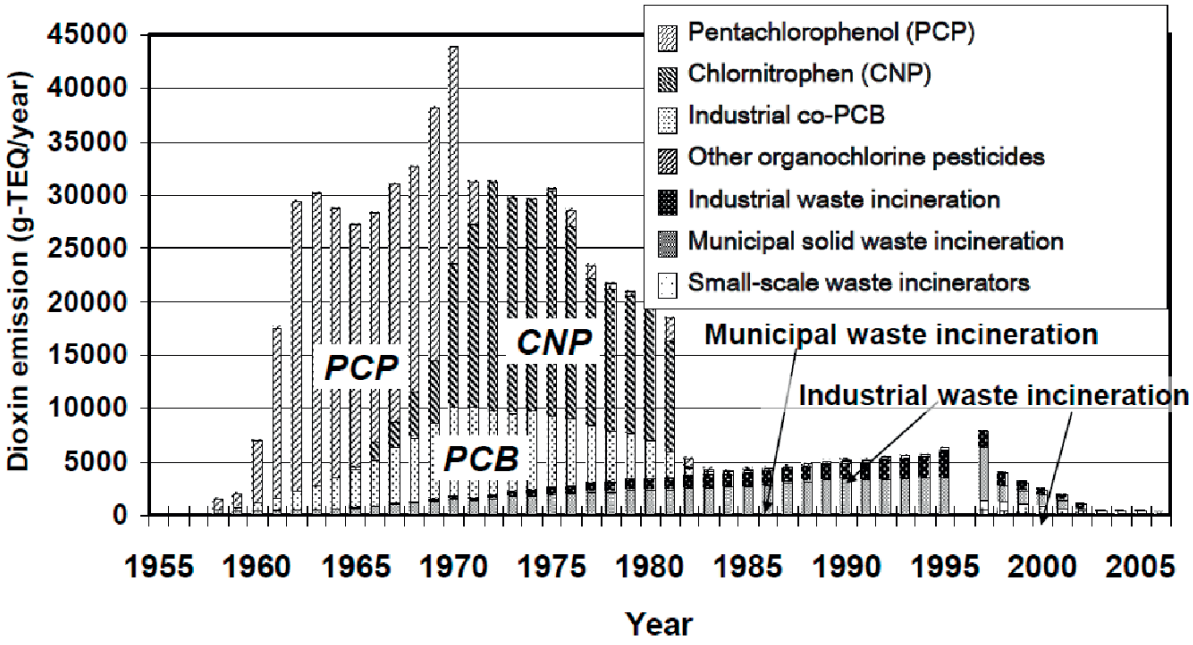
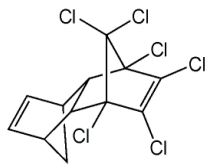
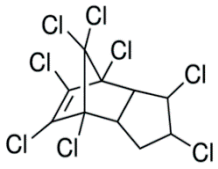
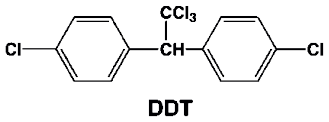
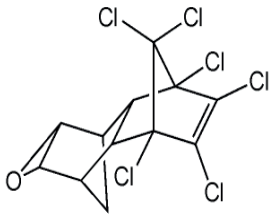


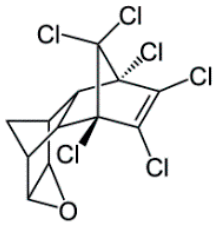
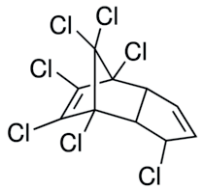
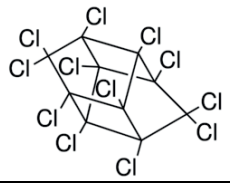
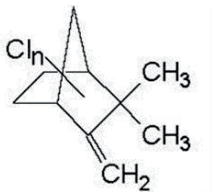
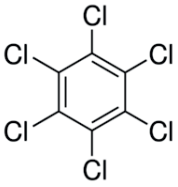
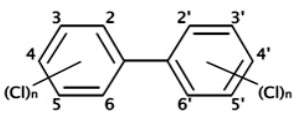
Fig. 2.1 Japanese dioxin emission inventory (WHO-TEQ, 1998) (Weber et al. 2008)

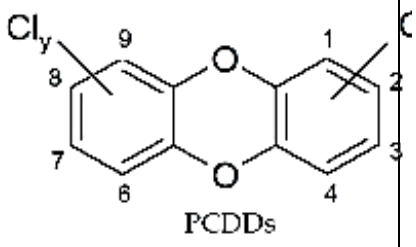
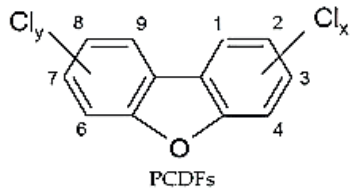
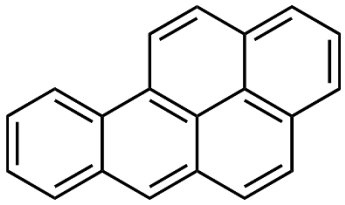
2.3.3 Sources of Major Chlorinated POPs

Types of POPs according to their source are categorized above and the sources of chlorinated POPs are listed in Table 2.2.

Table 2.2: Sources of major POPs.

POP chemical	Sources
Aldrin 	● Used to control pests dwelling in soil, such as termites, corn rootworm, wireworms, rice water weevil, and grasshoppers. ● Applied in agriculture against termites. ● Used to combat infestations in wood preservation.
Chlordane 	● An insecticide that has been used on agricultural crops for control of termites. ● wood preservative ● Protective treatment for underground cables.
DDT 	● Was used to protect the spread of vector borne diseases such as malaria, typhus. ● Widely applied on a variety of agricultural crops and for the control of disease vectors. ● Still used to control mosquito vectors of malaria in tropical countries.
Dieldrin 	● Used in agriculture for the control of soil insects and tropical disease vectors. ● Industrial uses include termite-proofing of plastics and rubber coverings of electrical and telecommunication cables of plywood and building boards, timber preservation, and as a termite barrier in building construction.

Endrin 	● Foliar (leaf) insecticide used mainly on field crops, such as cotton and grains. ● Employed as a rodenticide to control rodents such as mice.
Hepatachlor 	● An insecticide, used against soil insects and termites. ● Applied against cotton insects, grasshoppers, some crop pests. ● Used to combat malaria.
Mirex 	● Insecticide used mainly to combat fire ants, while being used against other types of ants and termites. ● Used as a fire retardant in plastics, rubber, and electrical goods
Toxaphene 	● Used on cotton, cereal grains, fruits, nuts and vegetables. ● In livestock it is used to control ticks and mites.
Hexachlorobenzene (HCB) 	● Used to treat seeds, as a fungicide ● a byproduct of the manufacture of industrial chemicals including carbon tetrachloride, perchloroethylene, trichloroethylene, and pentachlorobenzene ● Exists as an impurity in several pesticides including pentachlorophenol and dichloram.
Polychlorinated biphenyls (PCB) 	● used as heat exchange fluids in transformers and capacitors, ● as pesticide extenders, adhesives, dedusting agents, cutting oils, flame retardants, hydraulic lubricants, sealants, paints, and in carbonless copy paper

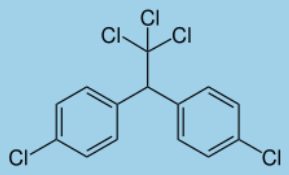
PCDD  PCDDs	• Emitted due to incomplete combustion during the manufacture of pesticides and other chlorinated substances. • Emitted mostly from the incineration of hospital waste, municipal waste, hazardous waste and also from automobile emissions, peat, coal and wood.
PCDF  PCDFs	• Produced unintentionally from the similar processes that produce dioxins, and also during the production of PCBs. • Detected in emissions from waste incinerators and automobiles.
PAH e.g.: Benzo-a-pyrene 	• Natural sources include forest and grass fires, oil seeps, volcanoes, chlorophyllous plants, fungi, and bacteria • Anthropogenic sources; petroleum, electric power generation, refuse incineration, home heating, production of coke, carbon black, coal tar, and asphalt and internal combustion engines

2.4 Sources of POPs in Sri Lanka

Sri Lanka became a signatory to the Stockholm convention on Persistent Organic Pollutants on 5th September 2001. To meet the obligations towards the convention, the United Nations Environment Programme (UNEP) and Global Environment Facility (GEF) facilitated a project for a national implementation plan for the control of POPs.

2.4.1.1 Sources of Organochlorine Pesticides in Sri Lanka

Trivia Fact: What was the first synthetic pesticide which was used in Sri Lanka on a large scale?
DDT. This was used immediately after the World War II in the late 1940's





DDT was followed by hexachlorocyclohexane (HCH) also called benzene hexachloride (BHC) to control the *Anopheles* malaria mosquito. Subsequently, with the success achieved in vector control, these pesticides were used in agriculture for control of pests to meet the post-war increasing demand for food. By the next decade, more toxic chemicals such as Aldrin, Dieldrin, Endrin were also included in the list of pesticides which were used indiscriminately for control of pests in the fields of agriculture, veterinary practice, public health and industry.

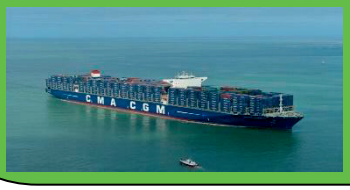
Table 2.3: Status of prohibition and import of POP pesticides in Sri Lanka (Adapted from: Persistent Organic Pollutants (POPs) Project, 2006, Ministry of Environment).

Name of pesticide	Year of prohibition/restriction of imports	Last imports	
		Amount (kg)/year	Year
Aldrin	1986	7,040	1986
Chlordane	1996	4,600	1994
DDT	1976	316,522	1976
Dieldrin	1992	1,100	1991
Endrin	1970	NA	-
Hepatachlor	1986	NA	-
Hexachlorobenzene (HCB)	Never been used	None	-
Mirex	Never been used	None	-
Toxaphene	1970	NA	-

NA- Not Available

Long range transport and accumulation in soil

Only limited data is available on POPs as they are either banned, not used for last fifteen years (Endrin, Hepatachlor, Toxaphene) or no records had been kept in Sri Lanka (HCB and Mirex). Recent detection of their residues in the seabed may be due to their persistence and excessive use in the distant past or due to long distance transport bound to particles from the sites of their use. It may also have been due to the sweepings of ships and containers arriving at harbour contaminated with POP pesticides. However, the source of contamination has not yet been identified.





These pesticides summarized in Table 2.3 were not manufactured in Sri Lanka, but were imported as ready-to-use products or technical materials for local formulation.

In Sri Lanka, with the implementation of the Control of Pesticides Act No.33 of 1980, there are no POP pesticides presently used in the fields of Agriculture, Public health, Industry or any other field as stated in the preliminary inventory of POPs pesticides in Sri Lanka, 2006 by the Ministry of Environment Sri Lanka. The prohibition of use of POP pesticides was initiated in early 1970's and was successfully completed in 1996 with the ban of Chlordane, which was the last POP pesticide used in Sri Lanka.

According to the Control of Pesticides Act No. 33 of 1980 and regulations made there under the Office of the Registrar of Pesticides is entrusted with the mandate of enforcement of control on import, packing, labeling, storage, formulation, transport, sale and use of pesticides through registration of pesticides. More information on the activities carried out by the Office of the Registrar of Pesticides can be for at https://doa.gov.lk/rop-home-3/

2.4.2 Sources of PCBs in Sri Lanka

Sri Lanka has ratified the Basel Convention (http://www.basel.int/; treaty to control the transboundary movements of hazardous wastes and their disposal) and Stockholm Convention (www.pops.int/). These treaties obliged to find environmentally sound solutions for PCB wastes. Therefore, the inventory of PCB will also be used to find preventive measures for PCB wastes subjected to transboundary movement through Sri Lanka. PCB oils were initially used as dielectric fluids for use in electrical equipment such as transformers, capacitors, circuit breakers, voltage regulators etc.

A survey conducted by UNDP Sri Lanka shows that 48% of the transformers available were manufactured on or before 1986 and are contaminated with PCBs. Recent studies indicate that

around 17,528 transformers owned by the Ceylon Electricity Board (CEB) and 2,700 owned by Lanka Electricity Company Private Ltd, are contaminated with PCBs.

2.4.3 Sources of PCDDs and PCDFs in Sri Lanka

PCDDs and PCDFs are considered as major unintentional persistent organic pollutants which are produced from anthropogenic activities. In Sri Lanka there are several activities that could lead to the production of these by-products especially in the open-air burning. There is inadequate legislation in the country for controlling such activities.

The main sources of release of PCDD/PCDFs in Sri Lanka were identified as:

1. **Waste Incineration** comprises of seven source categories of waste incinerators, which are divided into classes in each category and corresponding default emission factors by every class.
2. **Ferrous and Non-Ferrous Metal Production** comprises of twelve source categories for the production of metals and metal alloys including recycling operations, which are divided into classes in every category and corresponding default emission factors by each class.
3. **Heat and Power Generation** comprises of five source categories of large and small installations using fossil fuels, biomass or gas, which are divided into classes in every category and corresponding default emission factors by each class.
4. **Production of Mineral Products** comprise of seven source categories of processes to manufacture mineral products, which are divided into classes in every category and corresponding default emission factors by each class.
5. **Transport** comprises of four source categories including road and ship transport, which are divided into classes in every category and corresponding default emission factors by each class.
6. **Open Burning Processes** comprise of two source categories of burning biomass or waste without technical equipment, which are divided into classes in every category and corresponding default emission factors by each class.
7. **Production and Use of Chemicals and Consumer Goods** comprises of eight source categories of various industrial activities, which are divided into classes in every category and corresponding default emission factors by each class.
8. **Miscellaneous** comprise of an array of five source categories that do not match the description of any other source group, which are divided into classes in every category and corresponding default emission factors by each class.

9. **Disposal and Landfill** comprises of five source categories related to waste disposal, which are divided into classes in every category and corresponding default emission factors by each class.
10. **Contaminated Sites and Hotspots** comprise of thirteen source categories that should be noted in the inventory where contamination might have occurred. In the National Implementation Plan (NIP) process, these sites would be further assessed and classified.

Toxic Equivalent Factor (TEF) and Toxic Equivalent (TEQ)

In order to calculate a TEQ, a toxic equivalent factor (TEF) is assigned to each member of the dioxin and dioxin-like compounds category. The TEF is the ratio of the toxicity of one of the compounds in this category to the toxicity of the two most toxic compounds in the category. E.g.: The value for 2,3,7,8-subst. Cl_6DD is 0.1.
A TEQ is calculated by multiplying the actual mass in grams of each dioxin and dioxin-like compound by its corresponding TEF (e.g., 50 grams X 0.1 TEF = 5 gram TEQ) and then calculating the sum of the TEQs of all the compounds. The number that results from this calculation is referred to as grams TEQ.
For example, consider the following 6 g mixture:





1 g of compound X, with a TEF of 1
2 g of compound Y, with a TEF of 0.2
3 g of compound Z, with a TEF of 0.5.
The TEQ of this mixture would be: (1g x 1) + (2g x 0.2) + (3g x 0.5) = 2.9g TEQ

2.4.3.1 Source Group 1 - Waste Incineration

This includes seven types of waste incineration categories such as municipal solid waste, sewage sludge, hazardous waste, light fraction shredder waste, medical waste, waste wood and waste biomass, and animal carcasses. A considerable Toxic Equivalent (TEQ) observed in source categories from the emissions from hazardous waste incineration, medical waste incineration, waste wood and waste biomass incineration and destruction of animal carcasses in Sri Lanka.

2.4.3.2 Source Group 2 - Ferrous and Non-Ferrous Metal Production

Activity rates for twelve categories of metal production are covered under source group 2. They *are iron ore sintering, coke production, iron and steel production, copper production, aluminum production, lead production, zinc production, brass and bronze production, magnesium production, other non-ferrous metal production, shredders and thermal wire reclamation*. A considerable Toxic Equivalent (TEQ) observed in source categories from the

emissions from iron and steel production (iron and steel, foundries, hot-dip galvanizing), copper production, aluminum production, lead production, zinc production and brass and bronze production in Sri Lanka.

2.4.3.3 Source Group 3 - Power Generation and Heating

Source group 3 contains five categories of power generation and domestic heating and cooking. According to statistics of the National Energy Balance, 2013, emissions from coal, fuel oil, diesel, residual oil, naphtha and biomass from power generations contribute for dioxin and furan release into air. Other than that, household cooking / heating using biomass (firewood) releases PCDD/PCDF to air and residue of 13.179 g TEQ/year and 2.5 g TEQ/year, respectively. Then household heating and cooking with fossil fuels (kerosene and liquid petroleum gas) recorded total of 0.062 g TEQ/year release of PCDD/PCDF to air and estimated emission of PCDD/PCDF from biogas cooking is equal to 0.0001 g TEQ/year.

2.4.3.4 Source Group 4- Mineral Products

A total of 0.05 g TEQ/year was released to the air due to cement manufacturing in 2013. According to the Mineral Yearbook 2013, a total of 167,064 tons of lime was produced in 2013. This resulted in 1.671 g TEQ/year of total emissions from unintended byproducts to air. Brick production in Sri Lanka is a rural industry which mainly uses biomass waste material such as sawdust and paddy husk as the energy source. An estimated 6176 million number of bricks were produced in 2013 giving an estimated emission level to air of 0.151 g TEQ/year, while the amounts associated with products and residue are 0.045 and 0.015 g TEQ/year, respectively. The production of glass (single glass manufacturer) in Sri Lanka in 2013 was 87,330 tons. So the estimated PCDD/PCDF emission to air, resulted in 0.001 g TEQ/year emission. There are about 8 large scale ceramic product manufacturers in the country according to the report of the Export Development Board, 2013. A total of 106,479 tons of ceramic products were manufactured resulting in 0.002 g TEQ emission of PCDD/PCDF to air.

Due to the rapid development in road projects carried out during the recent past, the usage of asphalt has been rapidly increasing. In 2013, the asphalt plants of the Road Development Authority (RDA) have produced a total of 257,453 tons' asphalt. The rest, 237,438 tons, were produced at plants owned by private sector contractors. Most of these plants have no or poor gas cleaning systems and hence, an amount of 0.035 g TEQ/year was estimated PCDD/F to be released to air from asphalt mixing in 2013.

2.4.3.5 Source Group 5 – Traffic

Petrol and diesel are the two common fuels used in vehicles with 4-Stroke and 2-Stroke engines. The vehicles with catalytic converters have usually a lower emission of PCDD/F compared with other types. The effectiveness of catalytic converters tends to diminish with time especially due to the fact of high Sulphur content in gasoline used in Sri Lanka. Only unleaded petrol is used in Sri Lanka and octane number higher than 92 are solely used by vehicles with catalytic converters. The estimated PCDD/F emissions from petrol 4-Stroke engine vehicles with catalytic converters are 0.0001 TEQ/year and without catalytic converters 0.044 TEQ/year. The 2-Stroke vehicles lead to 0.514 TEQ/year which also burn petrol without catalytic converter.

The estimated emissions from diesel vehicles is 0.165 g TEQ/year. Consequently, a total of 0.7321 g TEQ/year PCDD/F was estimated to be emitted from vehicles in 2013.

2.4.3.6 Source Group 6 - Open Burning Processes

Open burning processes can be categorized as *biomass burning, forest fires and waste burning and accidental fires*. NIP plan updates suggests that, the biomass burning has reduced significantly. It is all because waste from rice mills and sawmills are now used in industries as fuel and practice of Chena cultivations has almost ceased to exist. Burning of straw is banned and farmers are required to use straw as a supplementary soil conditioner. According to the Forest Department statistics, about 40 ha of forest were destroyed by fire and out of them 10 ha can be considered as savanna (mixed woodland grass ecosystem characterized by trees being far apart to give a spaced canopy). This would have resulted in 0.001 g TEQ/year emission of PCDD/PCDF to air.

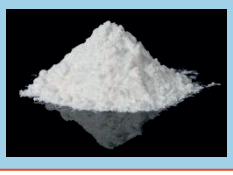
The main strategy adopted for dumping municipal waste is land filling and open dumping. The waste resulted after composting was assumed to be end up in landfills and open dumps. Therefore, an estimated 119,044 tons of waste were burnt at dump sites. Therefore, it was estimated that a total of 35.713 g TEQ/year and 1190 g TEQ/year of PCDD/PCDF were released respectively, to the environment by open burning of these wastes.

2.4.3.7 Source Group 7- Production and Use of Chemicals and Consumer Goods

Pulp and paper production, chlorinated chemicals, petroleum production, textile production and leather refining are the sources of PCDD/F in Sri Lanka. A recycled paper pulp processing facility at the Board of Investment of Sri Lanka (BOI) processed 3480 tons of pulp resulting in 0.01 g TEQ/year release into products during 2013. In addition, triclosan is a currently used chemical containing PCDD/PCDF in soap, toothpaste, detergents and cleaners.

There is only one petroleum refinery running in Sri Lanka and resulted in 0.001 g TEQ/year emission of PCDD/F to air due to fuel burning in 2013. Textile and apparel is a major industry in Sri Lanka and recorded 173 tons of textile dyes with low end technology and 13624 tons in mid-range technology plants and was given a total release of PCDD/PCDF to water is 0.02 g TEQ/year in 2013. These dyes are generally toxic and are released to water through factory effluent. Generally, 8400 tons of leather was refined during 2013, giving a total release of 0.171 g TEQ/year to products. In the leather industry, in addition to PCDF/PCDD, chromium is a significant waste material released in the process but comes under heavy metals.

Do you know? :
TiO_2 is used as a pigment in the paper industry. TiO_2 is responsible for 0.001 g TEQ/year emission of PCDD/PCDF to residues.



2.4.3.8 Source Group 8- Miscellaneous

This source group includes crematoria, smoke houses, dry cleaning establishments and tobacco smoking. During 2013, 0.028 g TEQ/year of PCDD/PCDF release to the air due to cremations. Smoke houses are used for production of copra and rubber sheets where firewood is consumed for energy. The respective emissions of PCDD/PCDF to air and residue due to the smoking of copra and rubber is 0.041 and 1.376 g TEQ/year. Dry cleaning of textiles using organic solvent (tetrachloroethylene) transfers the POPs in textiles to the solvents. It has been observed that about 30 % of the solvent used in dry cleaning ends up in distillation residue and recorded to release a 0.001 g TEQ/year of unintentional byproducts. A 4034.59 million sticks of cigarettes have been produced according to the information obtained from Ceylon Tobacco Company Tobacco smoking refers to cigarettes and ‘beedi’ a small brown cigar which accounts for 0.0005 g TEQ/year release of PCDD/F to air.

2.4.3.9 Source Category 9 – Waste Disposal / Landfill

This source category underlines municipal solid waste (MSW) disposal, land filling and open dumping. About 1,190,448 tons MSW end up in landfills and open dumps. This would result in 0.060 g TEQ/year and 5.952 g TEQ/year release of PCDD/PCDF to water and residue, respectively.

2.4.4 Summary of PCDD/F Status in Sri Lanka

Table 2.4 gives the overall summary of the unintentional byproduct (UPOP) inventory for the year 2013.

1. Accordingly, the highest contribution for UPOP emission came from the source category of waste incineration, where burning of healthcare waste was the major contributing factor.
2. The second highest contribution came from open burning that comprised household and agricultural waste burning.
3. The heat and power generation were the third highest emission group.

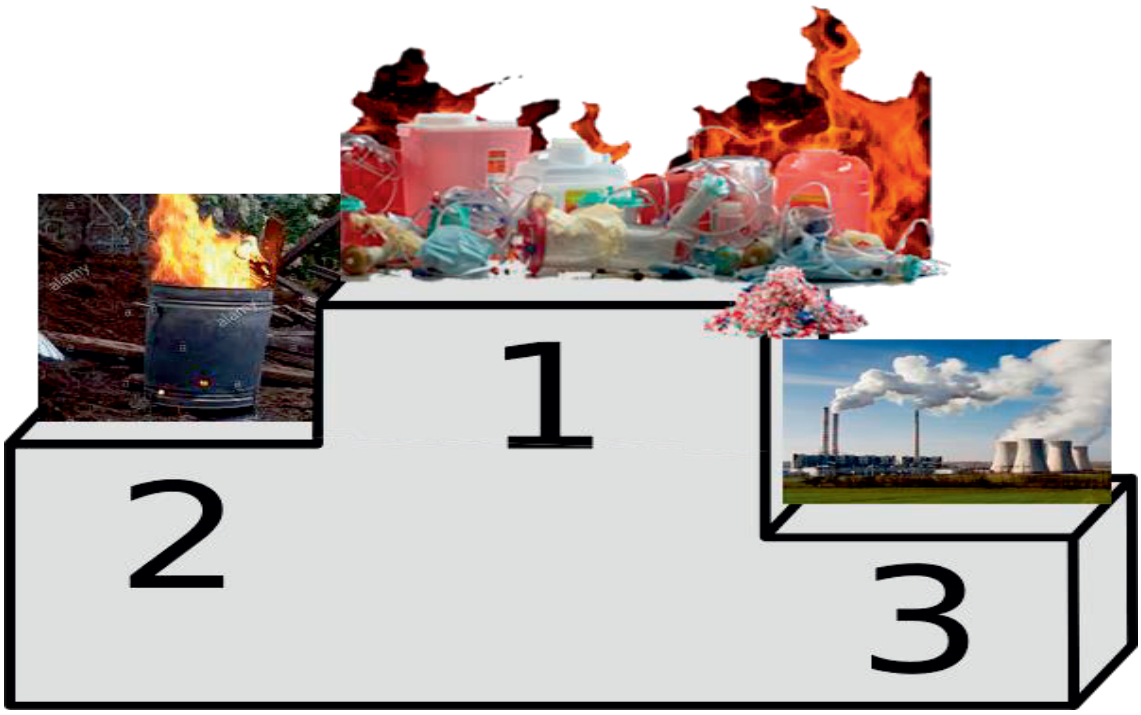


Fig. 2.2 Ranking of PCDD/F emission sources

Table 2.4: Summary of UPOP inventory 2013

Source group	**Annual Releases (g TEQ/year)**				
	Air	**Water**	**Land**	**Product**	**Residue**
Waste Incineration	58.5	NA	NA	NA	18.6
Ferrous and Non-Ferrous Metal Production	1.9	NA	NA	NA	5.1
Heat and Power Generation	28.6	0.0	NA	NA	2.6
Production of Mineral Products	1.9	ND	NA	NA	NA
Transportation	0.7	NA	NA	NA	NA
Open Burning Processes	49.4	ND	1.6	NA	NA
Production of Chemicals and Consumer Goods	ND	ND	ND	0.2	ND
Miscellaneous	0.152	NA	NA	NA	1.4
Disposal	0.0	0.1	NA	5.2	6.0
Identification of Potential Hot-Spots	ND	ND	ND	ND	ND
Total	**141.3**	**0.1**	**1.6**	**5.5**	**33.7**
Grand Total	**182 (g TEQ/year)**				

NA= not available, ND = not detected

3 Occurrence and Concentrations

3.1 Occurrence and Concentration of PBT chemicals

3.1.1 Aldrin

Aldrin is a chlorinated pesticide that controls soil insects such as termites, corn rootworms, rice water weevils, and grasshoppers. Crops such as corn and potatoes commonly protected by aldrin. In addition, aldrin protects wooden structures from termite attacks.

DICTIONARY

Hydrophobicity: the physical property of a molecule (known as a hydrophobe) that is seemingly repelled from a mass of water.

Aldrin is easily broken down to dieldrin by flora and fauna. As a result, residue of Aldrin is rarely found in food and animals, and even if found it is only in small amounts. Strong binding to soil particles causes it to show resistance to leaching into groundwater. It is mainly lost from soils through volatilization. Due to its persistence and hydrophobicity, Aldrin bioconcentrates, mainly as dieldrin.

It is reported that Aldrin can be stable in the presence of organic and inorganic alkalis, dilute acids, and hydrated metal chlorides (Budavari *et al*., 1989; IARC, 1974a; Lewis, 1993).

There is a high probability of finding aldrin and dieldrin residues in soil rather than in water. The present occurrence of aldrin in the environment is not known. However, it is expected that it may be lower now compared to the past as the manufacture and use of aldrin were stopped in 1974 in the United States.

3.1.2 Chlordane

DICTIONARY

Lipophilicity: the ability of a chemical compound to repel water and dissolve in fats, oils, lipids, and non-polar solvents

Chlordane is a broad-spectrum insecticide that is used on vegetables, small grains, maize, other oilseeds, potatoes, sugarcane, sugar beets, fruits, nuts, cotton, and jute. It was also utilized extensively controlling termites. Chlordane has a low solubility in water, and has a high solubility in organic solvents. It has a semi-volatility which results in atmospheric partition. It readily binds to aquatic sediments and undergoes bioconcentration in the fatty tissues of fauna as a result of its high partition coefficient.

The chemical properties of Chlordane (low water solubility, high stability, and semi-volatility) favor its long-range transport which results in its detection in Arctic air, water and organisms.

3.1.3 DDT

Do you know? : DDT was widely used during the Second World War to protect troops and civilians from the spread of malaria!



After World War II, DDT was mainly utilized on a variety of crops and to control vectors of disease which is done even to the present day. However, a developing interest among environmentalists about the negative environmental effects, especially on wild birds, led to severe bans and restrictions in many developed nations in the beginning of the 1970s decade. The crop which demanded the most use of DDT has been on cotton which accounted for more than 80% of USA use before being banned in 1972. However in despite of the above, DDT is still currently used to control malaria mosquito vectors in numerous nations.

DICTIONARY

Ubiquitous: present, appearing, or found everywhere

DDT is has a very low solubility in water and has a very high solubility in most organic solvents DDT has a semi-volatility which results in atmospheric partition. It has a ubiquitous presence in the environment with residues even being detected in the Arctic. It has a lipophilic nature (binds readily to lipid substances) and partitions easily into the fatty tissues of all living organisms and has been demonstrated to show bioconcentration and biomagnification. DDT breaks down into 1, 1-dichloro-2, 2-bis (4-chlorophenyl) ethane (DDD or TDE) and 1,1-dichloro-2,2bis (4-chlorophenyl) ethylene) (DDE), which are also ubiquitous in the environment and have greater persistence than the parent compound.

The above chemical properties of DDT favour its long-range transport which results in its detection in Arctic air, water and organisms. Virtually all organochlorine monitoring programs have detected DDT.

3.1.4 Dieldrin

The use of Dieldrin in agriculture was limited to the control of soil insects and several insect disease vectors but this latter use has been banned in a number of nations due to human health and environmental concerns. Principle contemporary uses are restricted to controlling termites, wood borers and against textile pests (WHO, 1989). Strong binding to soil particles causes it to show resistance to leaching into groundwater. It is mainly lost from soils through

volatilization and because of its persistent nature and hydrophobicity, Dieldrin undergoes bioconcentration.

Dieldrin has a half-life of approximately 5 years in temperate soils. This persistent nature, combined with a high solubility in lipids, provides the necessary conditions for Dieldrin to undergo bioconcentration and biomagnification in organisms.

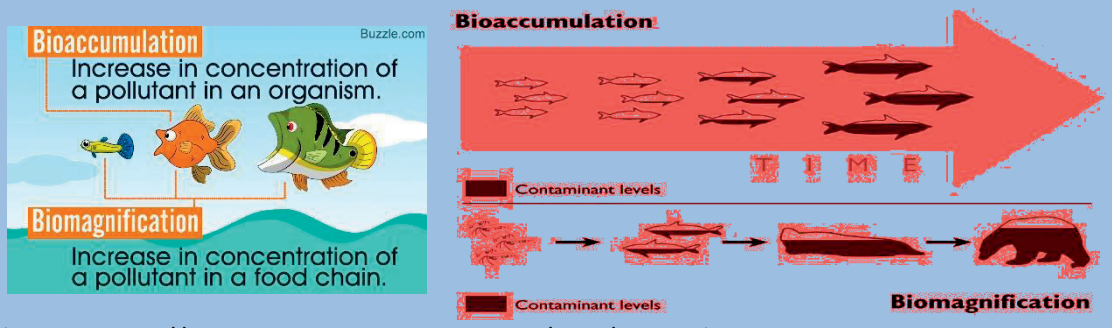
Bio magnification, Bioaccumulation and Bio concentration

These terms sound similar but have different meanings.

Bio-magnification: an increase in the concentration of a substance as you move up the food chain. This often occurs because the pollutant is persistent, meaning that it cannot be, or is very slowly, broken down by natural processes. These persistent pollutants are transferred up the food chain faster than they are broken down or excreted.

Bioaccumulation: where a concentration of a substance builds up in the tissues and is absorbed faster than it is removed, mostly by food.

Bio-concentration: A subset of bioaccumulation where absorption is directly from water



(Source: http://mercurypolicy.scripts.mit.edu/blog/?p=499)

Dieldrin bioconcentrates in factors of 12,500 and 13,300 with respect to guppies and sculpins, respectively. It is likely that Dieldrin undergoes bioconcentration rather than bioaccumulation by aquatic organisms. The chemical properties of Dieldrin such as insolubility in water, high stability, and semi-volatility favour its long-range transport which results in its detection in Arctic air, water and organisms.

Residues of Dieldrin have been detected in air, water, soil, fish, birds and mammals, including humans and human breast milk. Due to the rapid conversion of Aldrin to Dieldrin in the environment and in organisms, the levels of Dieldrin detected can be used to reflect the total concentrations of both compounds.

3.1.5 Endrin

Endrin is a foliar (used on leaves) insecticide used mainly on cotton and grains. It has also been used to control mice and voles (small rodents) as a rodenticide. It is quickly broken down by animals and does not accumulate in fatty tissues to the same extent as other compounds with similar structures (including its stereoisomer - Dieldrin). The formation of anti-12-hydroxyEndrin is considered to be the major route of metabolism of Endrin.

Volatilization is the main route of atmospheric entry, and in addition it can contaminate surface water from soil run-off.

Endrin is banned in many countries, including Belgium, Cyprus, Ecuador, Finland, Israel, Philippines, Singapore, Thailand, and Togo.

Endrin's chemical properties such as low water solubility, high stability in the environment, and semi-volatility favor its long-range transport, which causes its detection in Arctic freshwater. The general population is mainly exposed to Endrin through residues in food, however, the contemporary intake is generally below the acceptable daily intake of 0.0002 mg/kg body weight recommended by the Joint FAO/WHO Meeting on Pesticide Residues (JMPR).

3.1.6 Heptachlor



Heptachlor is a stomach and contact insecticide, utilized primarily against termites and soil insects. In addition, it is utilized against cotton insects, grasshoppers, some crop pests and to combat malaria. Heptachlor has a low solubility in water and has a high solubility in organic solvents. Its volatility causes it to partition into the atmosphere. It strongly binds to aquatic sediments and undergoes bioconcentration in the fatty tissues of living organisms. Heptachlor is broken down in animals to heptachlor epoxide, which has a similar toxicity to heptachlor, which may also be stored in animal fat.

Heptachlor has been banned in Cyprus, Ecuador, the EU, Portugal, Singapore, Sweden, Switzerland and Turkey. The WHO suggests that the major source of exposure of heptachlor to the general population is through food.

3.1.7 Hexachlorobenzene

Hexachlorobenzene (HCB) is a fungicide which was first introduced in 1945 for seed treatment, especially for control of bunt of wheat. HCB is produced as a byproduct of the manufacturing process of industrial chemicals such as carbon tetrachloride, perchlorethylene, trichloroethylene and pentachlorbenzene. Pentachlorophenol and dichloram contain HCB as a known impurity and is present as an impurity in others. HCB has a low solubility in water, and has a high solubility in organic solvents. Its volatility causes it to partition into the atmosphere. The insolubility in water, high stability, and semi-volatility of HCB favor its long-range transport, which causes its detection in Arctic air, water and organisms.

Do you know? : Bunt of wheat is a disease caused by two fungi *Tilletia tritici* and *T. laevis* .



3.1.8 Mirex



Mirex is a stomach insecticide with little contact activity whose main use was against fire ants in the southeastern United States, but was also used to combat leaf cutters in South America, harvester termites in South Africa, and has been investigated for possible use against yellowjacket wasps in the US. It plays a role as a fire retardant in plastics, rubber, paint paper, and electrical goods.

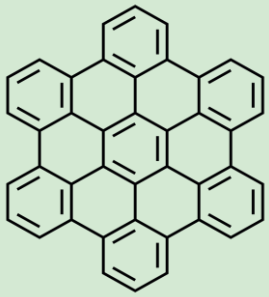
Mirex shows a high resistance to metabolism, has a low solubility in water, and undergoes bioaccumulation and biomagnification. Due to its low solubility, Mirex has a strong binding to aquatic sediments. Volatilization of Mirex from the surface of the soil into the atmosphere sometimes causes its deposition causing significant contamination of plant populations.

Increasing concentrations of Mirex have shown a reduction in germination and emergence in several plant species.

The uptake, accumulation and translocation of Mirex by a variety of plant species has also been observed. These results are questionable as lipophilic compounds such as Mirex are generally not known to demonstrate uptake and translocation by plants.

The insolubility in water, high lipid solubility, high stability, and semi-volatility favour Mirex's long range transport which causes its detection in Arctic freshwater and terrestrial organisms

Do you know? : Tobacco smoke contains about 200 PAH compounds



(WHO, 2008). The general population is generally exposed through food, especially meat, fish and wild game, while the intake is generally lower than established residue tolerances.

3.1.9 Toxaphene



Toxaphene is a nonsystemic and contact insecticide which was utilized primarily on agricultural crops such as cotton, cereal grains, fruits, nuts and vegetables. It also plays a role in controlling ticks and mites in livestock. Toxaphene has been in use since 1949 and was the most widely used insecticide in the USA in 1975.

Toxaphene has a low solubility in water and persists in soil with a half-life of up to 12 years. It has been observed to undergo bioconcentration in aquatic organisms and undergoes atmospheric transport. Toxaphene has been banned in 37 countries, including Austria, Belize, Costa Rica, Mexico, Dominican Republic, Egypt, the EU, India, Ireland, Singapore, Kenya, Korea, Panama, Brazil, Thailand and Tonga. Its insolubility in water, high stability, and semi-volatility favour its long range transport, and which causes its detection in Arctic air.

The general population is most likely exposed through food, however levels detected are usually lower than maximum residue limits.

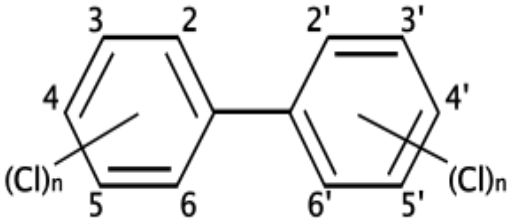
3.1.10 Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic Aromatic Hydrocarbons (PAHs) contain two or more fused aromatic rings containing only C and H as their name implies. PAHs substituted with functional groups are referred to as polycyclic aromatic compounds. They are originated due to the partial combustion of organic matter. They are highly lipophilic, less soluble in water and organic solvents hence and easily accumulated and persist in animal tissues.

Naphthalene, phenanthrene, fluoranthene, pyrene, benzanthracene, and benzopyrene can be listed as commonly identified PAHs. So far up to 100 PAH compounds has been identified as atmospheric particulate matter. Many of these compounds are carcinogenic, and genotoxic, mutagenic. They can be adsorbed in suspended particles and migrate into aquatic ecosystems. PAHs are less likely to be hydrolysable but susceptible to oxidation and photodegradation.

3.2 POPs Industrial chemicals

3.2.1 Polychlorinated biphenyls (PCBs)



Polychlorinated biphenyls (PCBs) are mixtures of organic aromatic chlorinated hydrocarbons which are extensively used as dielectrics in transformers and large capacitors, as heat exchange fluids, as paint additives, in carbonless copy paper and in plastics.

DICTIONARY

Vapour pressure:
A measure of evaporation of a substance

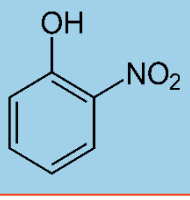
PCBs are highly valued in the industry due to chemical inertness, heat resistance, non-flammability, low vapour pressure, and high dielectric constant.

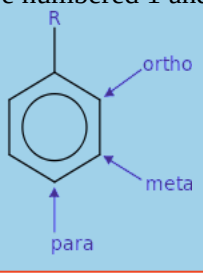
PCBs come in 209 possible structures, from three monochlorinated isomers to the fully chlorinated decachlorobiphenyl isomer. Generally, the water solubility and vapour pressure is inversely proportional to the degree of substitution, and the lipid solubility is proportional to the degree of chlorine substitution. PCBs are mostly expected to associate with the organic components of soils, sediments, and biological tissues, or with dissolved organic carbon in aquatic systems, rather than being dissolved in water.

PCBs undergo volatilization from the surface of water partly as a result of their hydrophobicity despite of their low vapour pressure, and PCBs may be distributed in the environment through atmospheric transport as a significant pathway.

Trivia: What is the ortho-position?

In ortho-substitution, two substituents occupy positions next to each other, which may be numbered 1 and 2.





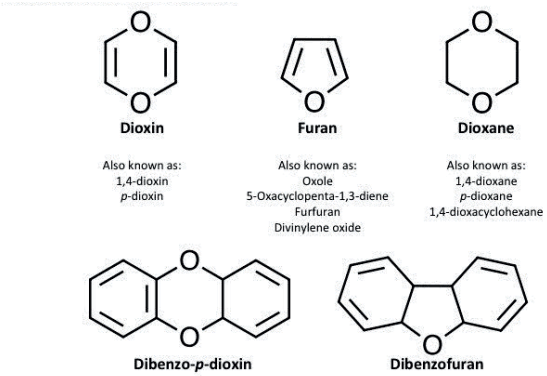
The toxicological effects of PCBs depends on the number and position of chlorine atoms, as substitution in the ortho position hinders the rotation of the rings. PCBs without ortho substitution are generally referred to as coplanar and all others as non-coplanar. Coplanar PCBs, like dioxins and furans, acts as tumor promoters by binding to AL-receptors in humans and may exert, thus, dioxin-like effects, in addition to AL-receptor independent effects which they share with non-coplanar PCBs.

Do you know? : Receptors are protein molecules in cells that receives chemical signals from outside a cell. The way a chemical interacts with these receptors may decide a biological response.

The breakdown of PCBs is dependent on the degree of chlorination of the biphenyl ring, with the persistence being proportional to the degree of chlorination. Insolubility in water, high stability, and semi-volatility favour their long range transport, which causes its detection in Arctic air, water and organisms. The general population is generally exposed through food, especially fish.

3.3 POPs By-products

3.3.1 PCDDs and PCDFs



Polychlorinated dibenzo-para-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are two groups of organic planar tricyclic compounds that have related chemical structures and properties. They may contain between one and eight chlorine atoms. There are 75 possible positional isomers for PCDDs and 135 positional isomers for PCDFs. They possess an extremely low solubility in water, are lipophilic and have increased persistence**.**

The chemical properties of each of the isomers have not been explained, further complicating a discussion of their properties which vary with the number of chlorine atoms present.

Dioxins or furans are not commercially produced, and they have no known use. They are unintentional by-products from the production of other chemicals such as pesticides and other chlorinated substances. PCDFs are a major contaminant of PCBs. Both dioxins and furans are connected to incineration processes, and the synthesis and utilization of a variety of chemical products. PCDDs and PCDFs have been detected in organochlorine pesticides and other organochlorine chemicals and emissions from the incineration of hospital waste, municipal waste, hazardous waste, car emissions, and the incineration of coal, peat and wood. Of the 210 various dioxins and furans, 17 are fully substituted in the 2,3,7,8-position and possess the dioxin toxicity.

PCDD/PCDF are considered to possess a high stability and persistence, for example the half-life of 2,3,4,7,8-PCDF in humans is approx.. 40 years and the PCDD/PCDF pattern in soils

contaminated by a chemical factory operating from 1830 to 1880 has not changed in the last 150 years (Balzer et al. 2007; Weber et al. 2018). Like many other organochlorines, the general population is exposed to these pollutants through food mainly of animal origin.

Their insolubility in water, high stability and semi-volatility favor their long-range transport causing them to be detected in Arctic organisms.

3.4 Heavy Metals

3.4.1 Mercury



Mercury is a highly toxic element that is found both naturally and as an anthropogenic effluent in the environment. Mercury may be present in the atmosphere as vapor. Mercury in water, soil, sediments or biota is in the form of inorganic salts or organic forms such as methylmercury (EPA, 1997a).For the global control of mercury the Minamata Convention has been established (http://www.mercuryconvention.org/).

Mercury may be released through industrial or mining activities and natural geological and ecological activities may bury, dilute, or erode the mercury deposits, resulting in the release of mercury from natural deposits into the surrounding ecosystem. A toolkit for inventory of mercury sources has been developed (UNEP 2017). In the northeastern Atlantic Ocean the concentrations of mercury in feathers of fish-eating seabirds have steadily increased for more than 100 years (Thompson 1992). With respect to North American sediment cores, the mercury concentration has multiplied about 3-5 times after industrialization compared to those found in older sediments. Due to human activities, some sites have been identified as methylmercury hot spots. Although scientists from USGS (United States Geological Survey) and elsewhere are beginning to unravel the complex interactions between mercury and the environment, a lack of information on the sources, behavior, and effects of mercury in the environment has become a barrier of effective management responses to the world's increasing mercury problem.

3.4.2 Lead



Lead is utilized to produce lead acid batteries, solder, alloys, cable sheathing, pigments, rust inhibitors, ammunition, glazes and plastic stabilizers. Even prepared food contains miniscule but significant amounts of lead. The exposure to lead increases when the water used for cooking, or the cooking utensils contain lead, or the food, especially if acidic, has been stored in lead-ceramic pottery-ware or lead-soldered cans. However the intake of lead from lead-soldered cans is decreasing as lead-free solders are becoming more common in the food processing industry.

Lead may be present in tap water to some extent as a result of its dissolution from natural sources, but mainly from household plumbing systems where the pipes, solder, fittings or service connections to homes contain lead. Polyvinyl chloride (PVC) pipes also contain lead compounds that can be leached into drinking water and result in high lead concentrations. The concentrations of lead in air depend on a number of factors, including the distance to major infrastructure and point sources. A study in Sri Lanka (CEJ 2011) discovered that 25% of paints in the market has dangerously high levels of lead with only 50% of paints with lead levels under the legal amount. Prior to 2002 in Sri Lanka, tetraethyl lead (TEL) was used as an additive to petrol as an anti-knocking agent before being banned.

Table 3.1 Summary of PBTs, their Concentration in Different media and relevant references

No.	Compound	Concentration in Air	Reference	Concentration in Water	Reference	Concentration in Food	Reference
1	Aldrin Dieldrin	Non-agricultural areas-0.06–1.6 ng/m^3	(WHO, 1989)	Aquatic environments and drinking-water - less than 10 ng/litre	(WHO, 1989)	Breast milk in in Europe and the USA - 0.5–11 µg/kg of milk	(WHO, 1989)
		Agricultural areas-1–2 ng/m^3	(WHO, 1989)	River sediments – up to 1 mg/kg	(WHO, 1989)		
2	Chlordane	Urban air - less than 0.1 to 60 ng/m^3	(ATSDR, 1989)	Drinking-water in USA below 0.1 µg/litre	(US EPA, 1987)		
		Rural air - 0.01 to 1 ng/m^3	(ATSDR, 1989)				
3	Dichloro-diphenyl-trichloro-ethane	Non-agricultural areas - <1–2.36 ng/m^3	(IPCS, 1979)	surface waters in the USA - 0.84 µg/litre	(IPCS, 1979)	human milk in 15 countries between 1976 and 1986 ranged from 2 to 380 µg/litre	(UNEP, 1988)

		Agricultural communities - 1 to 22 ng/m^3	(IPCS, 1979)	drinking-water in Czechoslovakia in 1972 and 1973 – 11 and 15 ng/litre	(IPCS, 1979)	In Egypt, in 1988, a mean daily intake of 960 µg was reported for the average adult.	(Abdel-Gawaad & Shams El Dine, 1989)
4	Endrin	Agricultural areas – mean level of 2.6 ng/m^3	(IPCS, 1992)	surface water in the USA in 1976–1980 - maximum value of 0.04 µg/litre	(IPCS, 1992)	US cities in 1978 - below 0.001 µg/kg of body weight	IPCS (1992)
5	Heptachlor and Heptachlor Epoxide	USA in 1971 - maximum level of 19.2 ng/m^3	(Stanley, 1971)	drinking-water at ng/litre levels	(Williams, 1976)	Human milk -men aged 25–30 were 0.007 µg and 0.184 µg, respectively	(Gunderson, 1988)
6	Toxaphene	Outdoor air - approximately 1 ppb	(ATSDR, 1996)				
7	Polychlorinated Biphenyls	Canada Northwest Territories 0.002 - 0.07 ng/m^3	IPCS (1993)	Germany Several rivers 5- 103 ng/litre	IPCS (1993)	Adults in the USA (1978) - 0.027 µg/kg body weight per day	

8	Hexachlorobutadiene	near chemical plant producing tetrachloroethene and trichloroethene (maximum 462µg/m^3)	(IARC,1979).	0.05–5 µg/litre in ambient water	(IARC, 1979)		
9	Lindane	0.01–0.7 ng/m^3- "unpolluted" remote areas	(Slooff & Matthijsen, 1988; ATSDR, 1989; Gustavson et al., 1990)	surface waters, levels of 0.01–0.1 µg/litre	(Slooff & Matthijsen, 1988; ATSDR, 1989; Gustavson et al., 1990)		
		urban and agricultural areas range from 0.1 to 2 ng/m^3	(Slooff & Matthijsen, 1988; ATSDR, 1989; Gustavson et al., 1990)			animal fats and eggs contain less than 10 µg of γ-HCH per kg	(Slooff & Matthijsen, 1988; ATSDR, 1989; IPCS, 1991).

10	Pentachloro-phenol	Finnish snow samples ranged from 1.49 to 136.0 µg/m^3	(Paasivirta et al., 1985)	Canadian water samples - non-detectable to 7.3 µg/litre	(WHO, 1987)	food samples from school kitchens - in positive samples was 6.3 µg/kg	(Veningerová et al., 1994)
				PCP concentrations in drinking-water are usually in the range of 0.01–0.1 µg/litre	(WHO, 1987)		
11	Chromium	Ambient air at most stations in the USA - generally below 300 ng/m^3		The natural total chromium content of surface waters is approximately 0.5–2 µg/litre , dissolved chromium content 0.02–0.3 µg/litre	(Slooff,1989), (Xingzhen, 1987), (Shiller,1987)	concentrations ranging from <10 to 1300 µg/kg	(Slooff,1989)
12	Manganese	ambient air near industrial sources - range from 220 to 300 ng/m^3	(Barceloux, 1999)	Levels in fresh water typically range from 1 to 200 µg/l	(Barceloux, 1999)		
		rural areas without point sources have been reported to	(Barceloux, 1999)	concentrations up to 1300 µg/l in neutral groundwater and	(ATSDR, 2000)	Fruits 0.20–10.38 mg/Kg, Nuts and nut products 18.21–46.83	(ATSDR, 2000)

		range from 10 to 70 ng/m^3		9600 µg/l in acidic groundwater			
13	Cadmium	Annual average concentrations in four cities in Germany in 1981–1982 were 1–3 ng/m^3	(JECFA, 1989)	unpolluted natural waters are usually below 1 µg/l	(Friberg et al., 1986)	Levels in fruit, meat and vegetables are usually below 10 µg/kg	(Galal-Gorchev, 1991).
				Drinking-water from shallow wells of areas in Sweden where the soil had been acidified contained concentrations of cadmium approaching 5 µg/l	(Friberg et al., 1986)	In 1980–1988, average cadmium levels in fish were 20 µg/kg wet weight	(Galal-Gorchev, 1991).

14	Iron	about 50–90 ng/m^3 ; at urban sites	(NRC,1979)	in rivers has been reported to be 0.7 mg/litre	(NRC,1979)	Liver, kidney, fish, and green vegetables contain 20–150 mg/kg	(WHO,2008)
15	Zinc	atmospheric zinc concentrations are typically between 10 and 100 ng/m^3	(Nriagu,1980)	natural surface waters - usually below 10 µg/litre	(Elinder,1986)	Protein-rich foods, such as meat and marine organisms, contain high concentrations of zinc (10–50 mg/kg wet weight), whereas grains, vegetables, and fruit are low in zinc (usually <5 mg/kg)	(Elinder,1986)

		urban areas commonly fall within the range 100–500 ng/m^3	(Nriagu,1980)	In groundwaters, 10 – 40 µg/litre	(Elinder,1986)		
16	Copper	Concentrations of copper determined in over 3800 samples of ambient air from 29 sites in Canada during 1984–1993 averaged 0.014 µg/m^3	(IPCS, 1998)	in surface waters ranged from 0.0005 to 1 mg/litre in several studies in the USA	(ATSDR, 2002)		
17	Nickel	in remote areas are in the range of 1–3 ng/m^3	(IARC, 1990).	average concentration in groundwater in the Netherlands ranges from 7.9 µg/litre (urban areas) to 16.6 µg/litre (rural areas)	(IPCS, 1991)	Higher median levels of nickel (0.1–0.4 mg/kg) were found in whole meal products	(Smart & Sherlock, 1987; Fødevaredirektoratet, 2000)

		concentrations in rural and urban air range from 5 to 35 ng/m^3	(IARC, 1990).				
18	Lead	average concentration in air of 0.2 µg/m^3	(WHO,2009)	drinking-water samples collected in five Canadian cities was 2.0 µg/l	(Dabeka, 1987)	In some countries, dietary intakes as high as 500 µg/day have been reported	(Galal-Gorchev ,1991)
						In Sri Lanka, a study found that the average concentration of lead in analyzed enamel paints was 11,600 parts per million (ppm).	(CEJ 2011)
19	Mercury	in air are in the range 2–10 ng/m^3	(WHO,2009)	Naturally occurring levels of mercury in groundwater and surface water are less than 0.5 µg/litre,	(Ware, 1989)	The average daily intake of mercury from food is in the range 2–20 µg	(Galal-Gorchev, 1991)

20	Arsenic	in remote or rural areas range from 0.02 to 4 ng/m^3	(USNRC, 1999)	In natural waters, including open ocean seawater, generally ranges between 1 and 2 µg/l	(Hindmarsh & McCurdy, 1986; USNRC, 1999)	levels ranging from 0.4 to 118 mg/kg have been reported in marine fish sold for human consumption, and concentrations in meat and poultry can be as high as 0.44 mg/kg	(Health and Welfare Canada, 1983).
		In urban areas, arsenic concentrations of 3–200 ng/m^3	(USNRC, 1999)			In Sri Lanka, agrochemical dependent varieties contain considerable amount (20.6 -540.4 µg/Kg) of arsenic.	(Jayasumana et al 2015)

4 Environmental Fate

Persistent bioaccumulative toxic chemicals (PBTs), also termed as *persistent environmental contaminants*, *persistent pollutants*, or *persistent toxic chemicals*, are chemicals which are resistant to environmental breakdown through processes such as chemical, biological, and photolytic means. They are known to persist in the environment, be transported in long-ranges, undergo bioaccumulation in tissues of humans and animals, undergo biomagnification in food chains, and have potential important influences on human health and the surrounding environment.

Tip: *Refer Chapter 3 for the differences between bioaccumulation and biomagnification*

4.1 Properties of PBTs

4.1.1 Persistence

Dictionary

Photolysis: the decomposition or separation of molecules by the action of light.

Naturally, many chemicals are spontaneously broken down by sunlight, undergo reactions with other environmental chemicals or subjected to metabolism by microorganisms. However some chemicals have characteristics that allow them to resist the above processes. These are termed as "persistent" and have the ability to accumulate in soil and aquatic ecosystems. Chemicals that have the ability to evaporate into air (volatilize) or dissolve in water can migrate considerable distances from their point of release. Humans and animals are more probable to be exposed to a chemical if it does not easily undergo degradation or is widely dispersed.

The convention on Long-range Transboundary Air Pollution (**LRTAP**) for POPs proposed "*half–lives*" in the four primary media of air, water, soil and sediment for the persistence of chemicals (Vallack et al; 1998). The structural chemistry of chemical compounds illustrate the chemical nature, reaction mechanism and reactivity. Chemical persistence to the environment, metabolic degradation and decomposition also depend on compounds' structure. Particularly, synthetic chemicals containing halogen atoms such as fluorine, chlorine, or bromine are often resistant to breakdown in the environment or inside living bodies.

Metals such as lead, mercury, and arsenic, are always persistent, since they exist as basic elemental atoms and cannot be further broken down into smaller units. E.g.: contamination of

air, soil, or drinking water with lead can finally result in significant exposures in fetuses, infants, and children, resulting in impaired brain development as they cannot be removed easily.

Explaining the concept of Half-life

Persistence is normally taken by the half-life (T ½) of a chemical in water, soil, or air. The half-life is *the amount of time necessary for a given amount of chemical released into the environment to decrease to one-half of its initial value*. For example, if 20 grams of a chemical with a half-life of 3 months were released into a lake and settled into the sediment, 10 grams would still be present in 3 months and 10 grams would have been degraded into various by-products. Three months later (Six months from release date), 5 grams of the original amount would still be present. It will continue halving every three months and so on.

According to the LRTAP POPs protocol, a chemical is persistent if it's,

Half-life in air > 2 days,

Half-life in water > 2 months,

Half-life in soil or sediments > 6 months

4.1.2 Bioaccumulation

Chemicals which accumulate in living beings from the environment, *so that their concentrations in body tissues continue to rise*, are called bioaccumulative chemicals. With respect to aquatic organisms like fish, bioaccumulation is sometimes called bioconcentration. The bioconcentration factor (BCF) is *a measure of the degree to which the concentration of a chemical in a fish's body is greater than the concentration in the surrounding water*. Decreased concentrations of a bioaccumulative substance in water may result in significantly higher concentrations in the tissues of fish at higher trophic levels of food chains, as well as in people or wildlife consuming them. Concentrations of volatile bioaccumulative substances will also be magnified in animals with lungs for respiration.

The potential for a chemical to undergo bioaccumulation can be foretold by analyzing whether the chemical preferentially dissolves in an organic solvent as opposed to water. If the concentration of a chemical in the organic solvent is more than 1000 times higher than its

concentration in water, when the chemical is added to an organic solvent and water mixture, the chemical is likely to bioaccumulate in organisms. If that concentration factor is greater than 5000, the chemical is highly likely to bioaccumulate.

Many bioaccumulative chemicals are soluble in fat so that they tend to exist in fat deposits or in the fatty components in blood plasma. This explains why fat-soluble bioaccumulative chemicals are often observed at increased levels in fat-rich breast milk. In addition, bioaccumulative chemicals may also be deposited elsewhere, including bones and muscles.

4.1.3 Bioaccumulation and Biomagnification

Bioconcentration is *the uptake of a chemical by an aquatic organism from water*. Bioaccumulation refers to *uptake from both water and food*.

The bioaccumulation factor (BAF) is the ratio of organism and water concentrations.

Biomagnification factor refers to the ratio of the concentration in the predator to that in the prey, notably on a lipid-adjusted basis (Vallack et al; 1998).

Organic chemicals are usually adsorbed to suspended or dissolved matter and called as ‘bioavailability’. However, octanol-water partition coefficient is the most frequently used measure of bioconcentration and bioaccumulation for non-polar organic compounds, which quantifies hydrophobicity as a determining factor of partition from water to lipid phases.

Table 4.1: Bioaccumulation and biomagnification of organochlorines in Arctic marine food chains (Adapted from controlling persistent organic pollutants–what next?) (Vallack et al; 1998).

	Water to zoo-plankton	Water to fish	Fish to seal	Fish to beluga	Fish to bird	Seal to bear
Toxaphene	6.7×10^4	2.6×10^6	0.38	4.6	-	-
HCH	9.3×10^3	3.0×10^4	1.5	1.4	0.7	9.3
Chloradane	2.6×10^6	5.3×10^7	7.3	9.4	0.33	6.6
DDT	$\geq 4.3 \times 10^5$	$\geq 1.4 \times 10^7$	20.2	9.8	8.5	0.3
PCB	1.9×10^6	4.8×10^7	8.8	8.0	5.8	7.4
HCB	1.2×10^5	9.6×10^6	0.2	3.0	7.5	15.6

PCB as Aroclor equivalents.

Explaining the concept of Octanol-water coefficient

Octanol-water coefficient is used as a useful indicator of bioaccumulation. In a mixture of oil and water, some chemicals dissolve in the oil more readily than water and vice versa. Similarly, some chemicals preferentially dissolve in the solvent, octanol, more readily than in water. The ratio of the concentration of a chemical in octanol with that of water in a mixture of octanol and water is called the octanol-water coefficient.

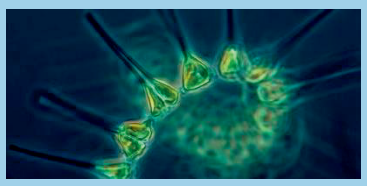
(Organisms to organism values are on a lipid/lipid basis)

4.1.4 Bioaccumulation Mechanisms

Due to the insolubility in water and the resistance to chemical and metabolic breakdown, most PBTs are liberated from organisms at slow speeds. As a result of this persistence, PBTs accumulate to elevated levels in living systems even at low environmental releases.

Do you know? : According to Swain et al., dissolved DDT, HCB and PCBs are directly absorbed from water by Phytoplankton and the above study suggested that DDT is accumulated directly by Arctic char through its gill membranes (Barrie et al; 1992).





However, in aquatic ecosystems, the primary route of entry to bodies is through the active uptake of PBT-contaminated particulate matter by the beginners (primary or secondary consumers) of the food chain (filter feeders and plankton) whereas at higher levels of the food chain, uptake through food is more important than direct absorption. Although the deposition and degradation process of PBTs in terrestrial ecosystems are not yet fully understood, it is well known that such chemicals can be absorbed directly through plant surfaces. For such an example, pine needles are found to be useful indicators of atmospheric contamination by organochlorines (George and Frear; 1996). The resistance to chemical and metabolic degradation explains the fact PBTs can become more concentrated further as they move up through food chains referred to as biomagnification. Biomagnification leads to concentrations of many orders of magnitude higher in top predators than in the environment. This is elaborated clearly in table 4.1 which shows more complex and longer processes in aquatic food chains than terrestrial food chains

Do you know? : For Arctic marine food chains, bioaccumulation factors (BAFs) from water to higher trophic level predators (seal, beluga, seabirds and bears) could be in **the order of 10^7 for toxaphene and HCB and as high as 10^9 for PCBs!!**

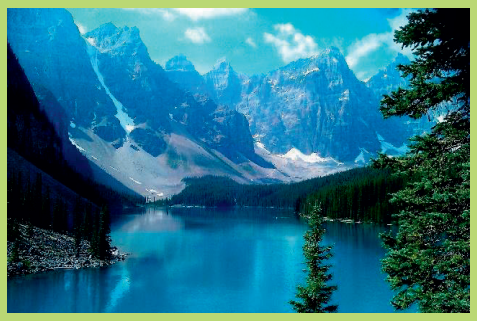




Case File 3

Measuring the bioaccumulation potential

Bioaccumulation level in a target species is dependent on the food structure of its habitat. For example, Baleen whales which skim the water for plankton are less contaminated than predatory species living in the same region (Mackay and Wania; 1995). It is observed, even different populations of same species, who live in habitats with equal contamination, will contain different levels of chemicals because of different feeding patterns. For example, it was discovered that in one Canadian walrus population, where levels of contamination with PCB, DDT, Toxaphene and chlordane were particularly high, the animals were feeding on seals as well as molluscs (Bidleman *et al*; 1989). They were, therefore, feeding at a higher trophic level than other less contaminated walrus populations which largely subsisted on molluscs. Biomagnification in a particular ecosystem can be studied using stable isotope analysis with the ratio of ^{15}N abundance relative to ^{14}N in an organism increasing on average 3–5 parts per thousand (%) compared with its source of dietary nitrogen (Goldberg;1975) due to the preferential excretion of the lighter isotope during metabolic processes. Using this technique, Kidd *et al.*(1995), showed that biomagnification through an unusually long food chain in Lake Laberge, Canada was the reason that lake trout and burbot contained amounts of toxaphene and other lipophilic contaminants several times greater than levels found in the same species inhabiting some other subarctic Canadian lakes (Finizio *et al*; 1997a).



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4.1.5 The Nitrogen Cycle

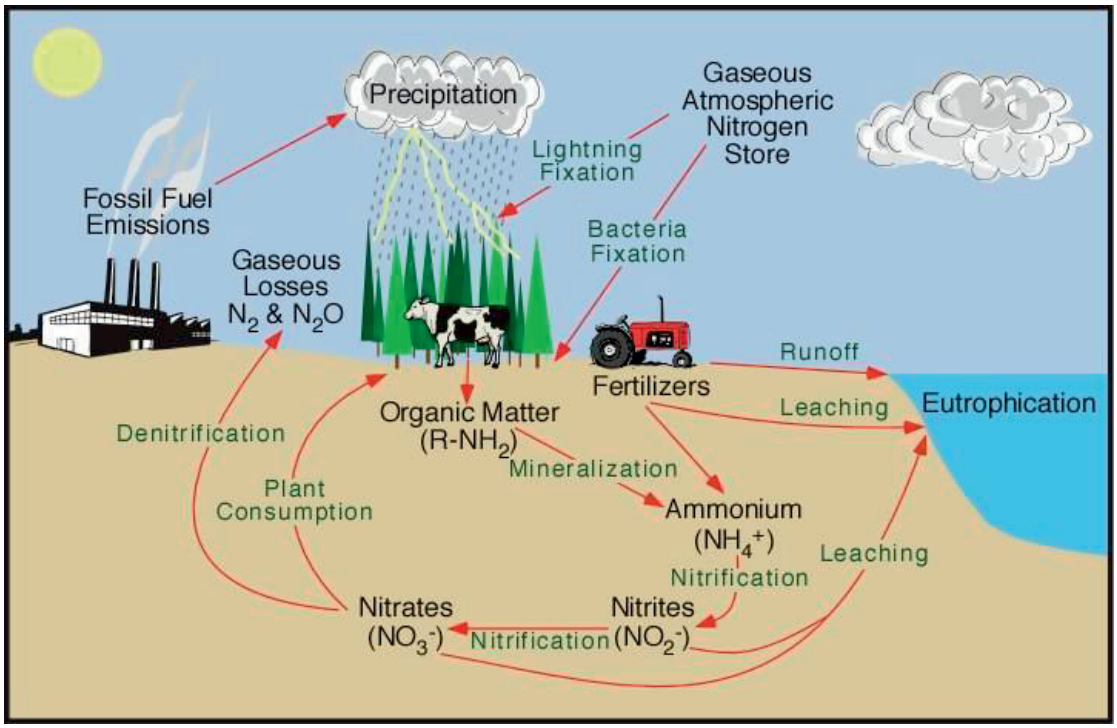


Fig. 4.1 The Nitrogen cycle (Adapted from PhysicalGeography.net)

The nitrogen cycle shown in Fig. 4.1 converts nitrogen into several chemical forms while circulating among the atmosphere, lithosphere, hydrosphere and biosphere. This conversion of nitrogen is fulfilled through biological and physical processes. Nitrogen fixation, ammonification (mineralization), nitrification, and denitrification are the most important stages of nitrogen cycle. The conversion of nitrogen gas (N_2), into nitrates and nitrites mostly through lightening and bacteria is called nitrogen fixation. Ammonification, which is also known as mineralization, is the process by which the organic nitrogen within the animal and plant remains are converted back into ammonium (NH_4^+) by bacteria and fungi. Ammonium is then converted to nitrate through nitrification, and it is performed primarily by soil-living and other nitrifying bacteria. For the completion of the nitrogen cycle, denitrification occurs by reducing the nitrates back into nitrogen gas.

The Nitrogen cycle explained above, plays a crucial role when determining some of the organochlorine levels in a particular organism. Also another study revealed that, a particular dioxin can have a half-life of few week s in rats and a half-life of 7-9 years in humans (Swain et al;1992). This indicates the difference in the ability of a different animal species to metabolize different PBTs or even different congeners (related chemicals) of the same group of PBTs. Therefore, in the risk assessment purpose, it is difficult to foretell the actual level of exposure of a receptor organism, for a given concentration of PBT in its environment, without

having extensive knowledge of the species' position in the food web in the ecosystem and of the PBT's persistence throughout the food chain concerned.

4.1.6 Criteria of Bioaccumulation

1. The bioaccumulation factor (BAF) or in fish, the bioconcentration factor (BCF) is the primary bioaccumulation criterion for all chemicals.
2. When considering non-polar hydrophobic organic chemicals, a secondary criterion is the octanol–water partition coefficient, if the molecular mass of the chemical is less than a certain critical value, variously estimated to lie between 600 and 1200, and if the substance is not broken down.

4.2 Toxicity



Fig. 4.2 DNA damage

Chemicals may possess a variety of toxic characteristics, resulting in a varied number of negative health effects. According to the Environmental Protection Agency, the toxicity rating of a potential PBT chemical is based on repeated exposures which result in human or environmental toxicity. Adverse impacts can include reproductive toxicity, genetic damage to DNA, neurological toxicity, developmental toxicity, cancer, or damage to immune system, among others.

Source: (EPA's criteria for PBTs are available at http://www.pbtprofiler. net/criteria.asp)

4.3 Sources of PBT releases into the environment

There are major industries associated with the release of PBT chemicals into environment which are summarized in table 4.2.

Table 4.2: Selected Industries and Processes Associated with PBTs

Manufacturing	Thermal processes	Certain products with PBT Impurities	Recycling processes
Production of chlorinated organic chemicals	Iron ore sintering for blast furnaces	Pesticide/herbicide application	Metal, paper and plastics recycling
Pulp and paper production	Primary copper smelting	Preservatives for wood/leather/textile	Sewage and paper sludge and effluent application on land
Oil refining and catalyst regeneration	Secondary scrap metal processing	Solvent use and application	Solvent and waste oil recovery
Chlorine production using graphite electrodes	Cement kilns	Industrial bleaching processes	Pentachlorophenol treated wood
	Mineral processing: lime, ceramic,glass, brick	Textile/wool/leather dying and finishing	
	Waste incineration: municipal, hazardous, medical/clinical		
	Coal and oil combustion vehicles and stationary motors		

4.4 The Environmental impact of PBTs

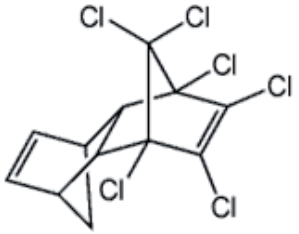
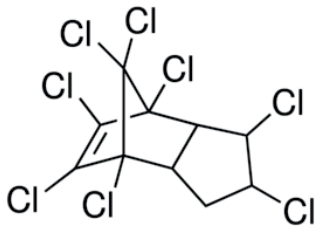
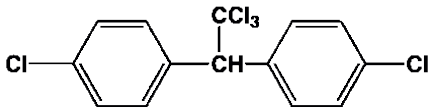
The environmental and human health impact of PBT chemicals are described below under the categories of;

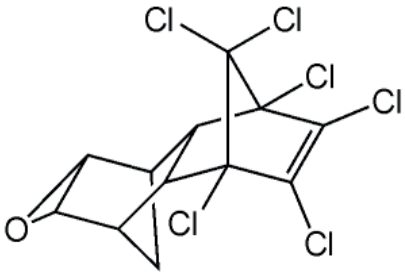
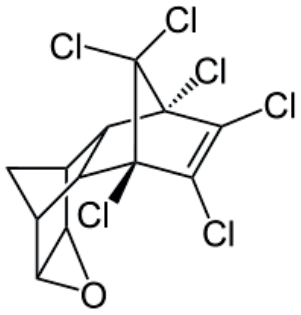
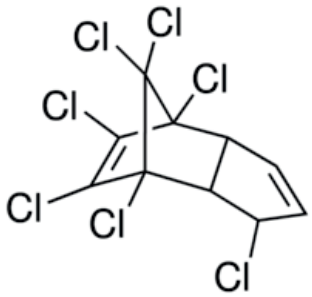
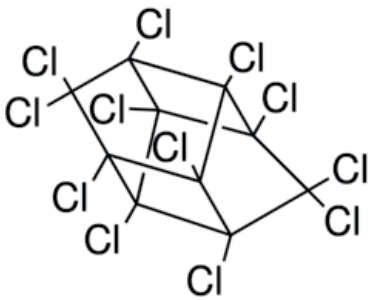
- Pesticides,
- Industrial chemicals,
- Unintentional by-products,
- Heavy metals.

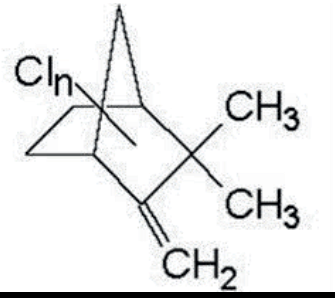
4.4.1 The Environmental Fate of PBT pesticides

The major source of POPs in Sri Lanka is agricultural pesticides. Sri Lanka has ceased the usage of PBT pesticides through government regulations and bans removing highly hazardous pesticides from agriculture. Table 4.3 shows some of those PBT pesticides banned by the Sri Lankan government.

Table 4.3: PBT pesticides and their environmental fate

PBT pesticide	Environment fate
Aldrin 	● Readily broken down to dieldrin by flora and fauna therefore aldrin residues are rarely found in foods. ● Strong binding to soil particles that results in resistance to leaching into ground water. ● Lost from soil through volatilization. ● Its conversion products are mainly persistent, hydrophobic and bioconcentratable.
Chlordane 	● Semi-volatile and binds to aquatic sediment. ● Bio-concentrates in the fat of organisms. ● Half-life in soil is one year. ● Lethal effects of chlordane on fish and birds vary according to species (e.g. kills mallard ducks bobwhite quail, pink shrimp)
DDT **(Dichlorodiphenyltrichloroethan**  **DDT**	● Semi volatile. ● Lipophilic, bio-concentrates and bio-magnifies. ● Breakdown products are present everywhere in the environment (e.g. DDD and DDE) and are more persistent than the parent compound. ● Highly persistent (50% remain in soil 10-15 years). ● Adverse impact especially for wild birds (e.g. egg shell thinning).

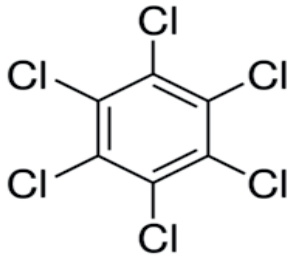
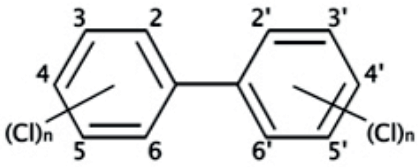
Dieldrin 	● Strong binding to soil particles that results in resistance to leaching into ground water. ● Lost from soil through volatilization. ● Persistent, hydrophobic and bio-concentrates. ● Half-life in soil is 5 years. ● Aldrin rapidly converts to dieldrin and its concentration alone is higher. ● Highly toxic to fish and other aquatic animals.
Endrin 	● Rapidly broken down by animals and does not accumulate in fatty tissues as the other compounds. ● Volatilization causes it to enter atmosphere. ● Contaminates surface water through soil-run off. ● Persist in soil for up to 12 years (long half-life). ● Highly toxic to fish (e.g. early stage hatching of sheepshead minnows).
Hepatachlor 	● Very low solubility in water, high solubility in organic solvents. ● Quite volatile and expected to partition into atmosphere. ● Binds to aquatic sediments. ● Bio-concentrates in the fat of organisms. ● Metabolized in animals to heptachlor epoxide which has similar toxicity. ● Responsible for the decline of several wild bird populations including Canadian Geese and American Kestrels.
Mirex 	● One of the most stable and persistent pesticides (half-life of 10 years). ● Bio-accumulates and bio-magnifies. ● Very insoluble in water hence binds strongly to aquatic sediments. ● Toxic to several species of plant, fish and crustaceans.

Toxaphene  	• Complex mixture of chemicals. • Very mobile for global distribution (e.g. atmospheric long range transport). • Persist for long periods in the soil (50% up to 12 years). • Highly toxic to fish (e.g. brook trout – weight loss and reduced egg viability).

Source: Department of Agriculture, Sri Lanka. (List of banned pesticides in Sri Lanka is available at https://www.agrimin.gov.lk/web/images/Pest_Management_Plan.pdf)

4.4.2 The Environmental Fate of PBT industrial chemicals

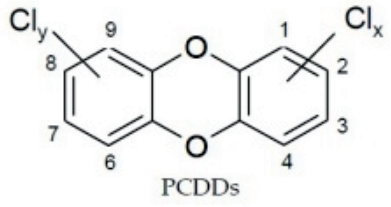
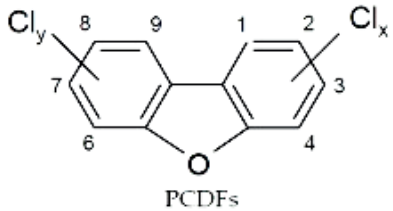
Table 4.4: PBTs industrial chemicals and their environmental fate

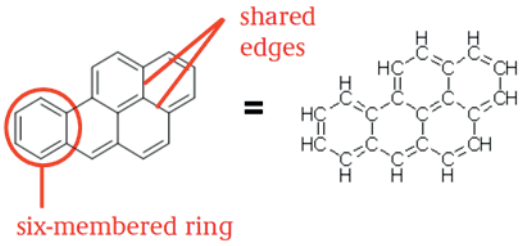
PBT industrial chemical	Environment fate
Hexachlorobenzene (HCB)  	• Low solubility in water but high solubility in organic solvents. • Quite volatile. • Very stable and resistant to breakdown. • Bio-concentrates in the fatty tissues of living organisms.
Polychlorinated biphenyls (PCB)  	• Present as a mixture of congeners (related chemical structures). • Water solubility and vapor pressure decreases as the degree of substitution increases. • Lipid solubility is proportional to chlorine substitution. • Associate with the organic compounds of soils. Sediments, biological tissues and dissolved organic carbon in aquatic systems. • Volatilizes from water surfaces due to low vapor pressure and hydrophobicity - atmospheric transport is significant in environmental distribution.

	● Persistent – depends on degree of chlorination. ● Toxic to fish, lethal at higher doses. ● Spawning failures at lower doses. ● Major damage – reproductive failure and suppression of immune system in animals.

4.4.1 The Environmental Fate of PBT Unintentional By-products

Table 4.5: PBTs unintended byproducts and their environmental fate

PBT by-product	Environmental fate
Polychlorinated dibenzo-p-dioxins (PCDD)  PCDDs	● Out of 75 different dioxins, 7 congeners persist in soil for 10-12 years.
Polychlorinated dibenzofurans (PCDF)  PCDFs	● Bio-accumulates in lipid rich tissues ● Bio-concentrates through food chains due to high solubility in fat. ● Persists in environment because of the high number of chlorinated components. ● Bio-magnifies in marine food chains.

Polycyclic Aromatic Hydrocarbons (PAH)  The structure of PAHs, using the example of benzo[a]pyrene	• Generated as mixtures of PAHs due to different substitutes. • Solid at room temperature, high boiling and melting points. • Therefore, strongly binds to soot, soil, or dust particles. • They have low vapor pressure, and very low solubility in water. • Lipophilic and fat solubility increases with the number of hydrocarbon rings.

In addition to the above traditional pesticides and compounds, the environmental fate of several compounds which include other halogenated POPs which include bromine such as polybrominated diphenyl ethers (PBDEs), polybrominated biphenyls (PBBs) and hexabromocyclododecane (HBCD). The sources of these persistent chemicals are diffuse, with a major source thought to be PBDE flame retardants leaching from everyday products such as textiles, computers, furniture foam, plastics, electronics, automobiles, and construction materials (Echols 2009). Exposure via eggs was shown to be a major pathway from e-waste recycling sites in China (Labunska et al. 2013, 2014).

In addition to brominated compounds, fluorinated POPs are listed under the Stockholm Convention as well. Examples such as (PFOS) perfluorooctane sulfonate, (PFOA) perfluorooctanoic acid and polyfluorinated alkylated substances (PFAS) cause widespread environmental pollution. These are known to undergo bioaccumulation in meat products (Lupton et al. 2014). Currently, more than 4000 PFAS are in use and they can accumulate in vegetables, fruits and grain, which can become an important exposure pathway for humans.

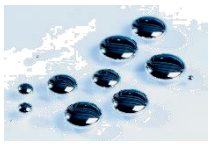
Table 4.6: Some PAHs and properties

Health hazard!  Environment hazard!  Warning 

Name	Molecular formula	Hazard designation	Hazard symbol
Benz[a]-anthracene	$C_{18}H_{12}$	Cancer causing possibility, high toxicity to aquatic organisms, with chronic effects	
Benzo[b]-fluoro-anthene	$C_{20}H_{12}$	Cancer causing possibility, high toxicity to aquatic organisms, with chronic effects	
Benzo[j]-fluoro-anthene	$C_{20}H_{12}$	Cancer causing possibility, high toxicity to aquatic organisms, with chronic effects	
Benzo[k]-fluoro-anthene	$C_{20}H_{12}$	Cancer causing possibility, high toxicity to aquatic organisms, with chronic effects	
Benzo[a]-pyrene	$C_{20}H_{12}$	Cancer causing possibility, genetic defects, impair fertility, and cause harm to the unborn child, high toxicity to aquatic organisms, with chronic effects	
Benzo[e]-pyrene	$C_{20}H_{12}$	Cancer causing possibility, high toxicity to aquatic organisms, with chronic effects	
Chrysene	$C_{18}H_{12}$	Cancer causing possibility, presumably cause genetic defects, high toxicity to aquatic organisms, with chronic effects	
Dibenz[a,h]-anthracene	$C_{22}H_{14}$	Cancer causing possibility, high toxicity to aquatic organisms, with chronic effects	
Naphthaline	$C_{10}H_8$	Cancer causing possibility, harmful if swallowed, high toxicity to aquatic organisms, with chronic effects	

4.4.2 The Environmental Fate of PBT Heavy Metals

Table 4.7: PBT heavy metals and their environmental fate

PBT heavy metal	Environmental fate
Lead 	• Widely distributed in environment where it was used as an additive in gasoline and in paint. • Now banned from use in gasoline (petrol) and paint. • Potent neurotoxin for children.
Mercury (includes organic and inorganic) 	• Persistent and undergoes bioaccumulation. • Contaminates bodies of many fish species • Widely used in industrial processes; causes developmental neurotoxicity mostly in children.
Cadmium 	• Occurs naturally. • Used in steel, plastics, batteries; found in cigarette smoke. • Causes lung cancer.
Arsenic 	• Environmental pollution by arsenic occurs as a result of natural processes such as volcanic eruptions, soil erosion, and human activities • Industrial applications are insecticides, herbicides, fungicides, algicides, sheep dips, wood preservatives, dye stuffs and in veterinary medicine • Used in medicine (treatment of syphilis, yaws, amoebic dysentery, and trypanosomaiasis) • Arsenic trioxide- used as an anti-cancer agent in the treatment of acute promeylocytic leukemia (US FDA)

4.5 Transport and Deposition Process of PBTs

Long-range transport

Long range atmospheric transport of PBTs has been associated with the inherent properties such as; 1.volatility, 2.resistance to photolytic, biological and chemical degradation.

Do you know? : PBTs have not been only detected at the site of emission even detected in remote regions such as open oceans, deserts, the Antarctic and Arctic regions where no significant local sources exist (UNEP;2012). DDTs and PCBs were first reported to be present in the Antarctic during 1960s and 70s (Stockholm convention; 2016).

More recently it has been realized that the concentrations are surprisingly high in polar regions given the remoteness from sources. In the Arctic, unexpectedly high levels of certain organochlorines were observed in seawater, precipitation, plankton and wild animals (North American Mosaic; 2015). Levels of PBTs found in Arctic marine ecosystems are such that there are concerns that biota, especially top predators and aboriginal peoples utilizing marine mammals and fish in their traditional diet may be adversely affected by chronic exposure to these pollutants





4.5.1 Global Distillation/Fractionation Effect

Regarding the long transport of PBTs, Wania and Mackay (1993), explained the theory behind the tendency of PBTs to migrate and deposit in polar regions, as a *'global distillation/fractionation effect'*. It suggests that high concentrations of some organochlorines are present in polar wildlife and **that pesticides used in warm climates become evaporated and transported to cooler areas where they will be subjected to condensation**. The 'Global distillation' term was first coined by Goldberg (1975) in relation to the transfer of DDT through the atmosphere from continents to oceans. This phenomenon is also termed as the *'cold condensation'*, *'cold finger'*, or *'cold trap'* effect.

More recently Wania and Mackay (1993) suggested that the physico-chemical properties of these chemicals and certain factors characterizing cold environments contribute to the long-term spatial distribution of organochlorine chemicals, location of release and transport pathways. The two major factors that affect the distribution pattern are;

- The volatility of a compound,
- The ambient temperature level.

In other words, their moderate volatility means PBTs tend to volatilize from tropical and temperate regions of globe, condense and then tend to remain in colder regions. The pattern of migration is termed the 'grasshopper effect' as they migrate to higher latitudes in a sequence of short leaps, rest and migrate again in in correspondence to seasonal temperature changes at mid-latitudes (Fig. 4.3).

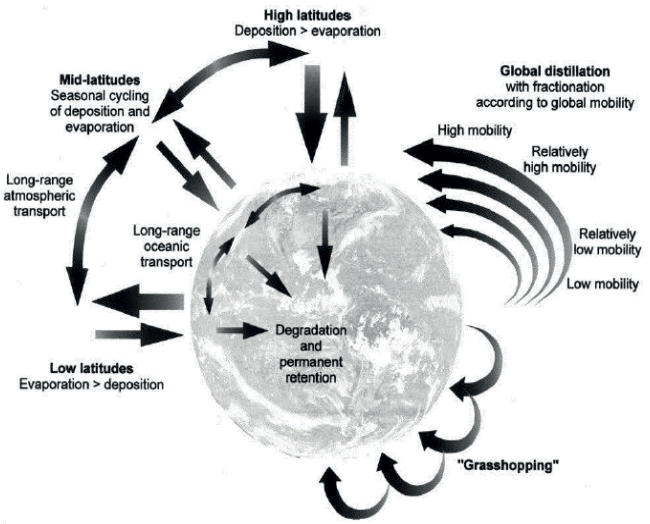


Fig. 4.3 POP global migration processes, (Adapted from controlling persistent organic pollutants–what next?) (Vallack et al; 1998).

Each and every PBT has its own unique condensation temperature or temperature range. It is also suggested that more highly volatile PBTs will tend to remain airborne and travel more rapidly towards the polar regions than less volatile PBTs. This phenomenon of separating out individual PBTs in the atmosphere along a temperature or latitude gradient based upon their degree of volatility is called 'global fractionation'. This indicates that, the past emissions can contribute to act as contaminant sources even after their releases have ended or declined due to the slow release from accumulated chemical reservoirs. Therefore, from the historical profiles of Arctic lake sediments, two main predictions of the cold condensation hypothesis have been supported;

I. More volatile organochlorines would show a preferential accumulation in polar regions,
II. The temporal trends in their deposition would be different from trends in temperate regions.

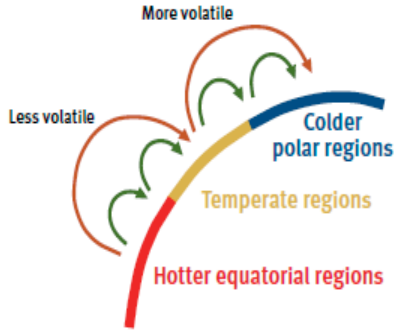


Fig. 4.4 The "grasshopper effect" (Adapted from: The North American Mosaic: An Overview of Key Environmental Issues)

For heavier PCBs and PCDDs, the impact around the point sources may range from a hundred meters to a few kilometers due to a less ability to undergo volatilization. These pollutants may be extremely persistent and exist in soils or sediments for decades and centuries. The half-lives of PCDD/Fs and PCBs in soils are decades to more than a century in the Central European climate (Weber et al 2018). This has led to management strategies in Italy and Germany prohibiting all cattle grazing grounds within a specific radius of steel and copper smelting plants.

4.5.2 Factors involved in PBTs' Transport and Deposition

There are several key factors involved in the potential of PBTs to condense, deposit and accumulate in cold ecosystems some of which are temperature dependent physical and chemical properties such as vapor pressure and water solubility. PBTs can exist both in the vapor phase and in a condensed form because of their semi volatility and are adsorbed onto small aerosol sized particles. Finizio *et al*., (1997b) suggested that, the octanol – air partition coefficient is an outstanding descriptor of the distribution. In a more descriptive state, cooler conditions favor greater adsorption onto atmospheric particulate matter which will then deposit more rapidly either by dry deposition or by precipitation scavenging (effective for particles than vapors). Cooler conditions promote enhanced adsorption of PBTs from vapor phase onto vegetation, soil, water, snow and ice at the Earth's surface.

DICTIONARY

Precipitation scavenging: The process by which rain or snow removes particulates from the atmosphere and deposits them on the ground surface.

DICTIONARY

Adsorption: The adhesion of an extremely thin layer of molecules to the surfaces of solid bodies or liquids *(Not to be confused with absorption)*

Then, accumulation will be enhanced under cooler conditions, due to reduced rate of PBT degradation (e.g. increased persistence and reduced tendency to revolatilize).

PBTs include a range of vapor pressures: more volatile compounds are transported to higher latitudes until they encounter sufficient low temperatures to cause them to become rapidly deposited from the vapor phase to particle phase. Therefore, global distillation/fractionation hypothesis predicts that these chemicals will become distributed according to a gradient by latitude and altitude according to their volatility. Very volatile compounds may never condense appreciably as sufficiently low environmental temperatures are absent, even if they are persistent.

4.5.3 Biomonitoring of PBTs

Special concern should be given towards children and developing fetuses with regard to PBT exposure. Children have a high vulnerability to toxic chemicals because of their unique physiological, developmental and behavioral features. The global biomonitoring data needed to measure the occurrence of PBTs in humans are not available as a whole, however some observations can be taken from more geographically localized studies:

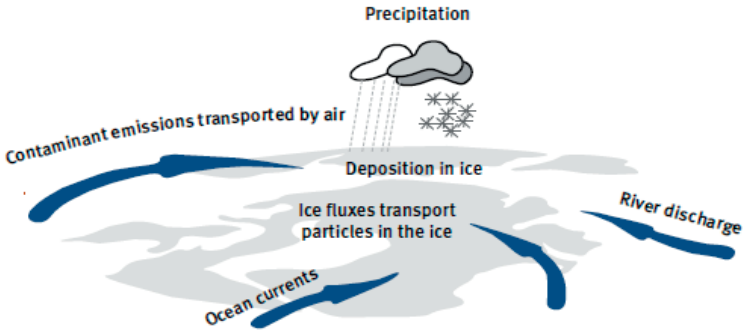


Fig. 4.5 Pathways of contaminants to the Arctic (Adapted from: The North American Mosaic: An Overview of Key Environmental Issues)

Case File 4

PBTs in Sri Lanka

Pesticides are globally used in agricultural and domestic purposes. However, some pesticides which kill pests through a biological mechanism such as organophosphates (the most commonly used pesticide worldwide) may also harm humans. Sri Lanka holds a high rank in the Asia Pacific Region regarding the adverse health effects related to pesticides. Annually the total number of pesticide accidents in Sri Lanka is around 20,000 of which 1,600 are fatal with 70% of this being suicide attempts (Source: Country Situation Report on Persistent Organic Pollutants (POPs) in Sri Lanka).

Acute and chronic exposure to PBT pesticides have caused severe health issues among Sri Lankans at present. Cancer, respiratory diseases, Parkinson's disease, renal failure and death by pesticide poisoning are some of the major health risks resulted by acute exposure to these pesticides. 1–4 People in low- and middle-income countries often experience acute and chronic exposure due to the widespread and unregulated use of pesticides (Knipe D.W; 2016). On the other hand, chronic exposure is higher in Sri Lanka due to settlement of rural families close to agricultural fields. The most recurrent disease reported in Sri Lanka since early 1990s, caused by PBT pesticides is kidney disease among paddy farmers in the North Central Province. Since then, it has spread to other agricultural communities in the dry zone. Though cadmium and fluoride are often cited as the main causative factors of Chronic Kidney Disease of unknown aetiology, PBTs too play a part in the aetiolog (Jayasumana et al. BMC Nephrology 2014).



Therefore, it is evident that persistent bioaccumulative and toxic substances are linked to biodiversity, international trade and climate change in any single country or world as a whole.

5 Measurement and Analysis of PBTs

According to United States EPA (Environmental Protection Agency) classifications, Persistent, Bioaccumulative and Toxic chemicals (PBTs) include Persistence Organic Pollutants (POPs) like poly-chlorinated biphenyls (PCBs), polychlorinated dibenzo-dioxins (PCDDs), polychlorinated dibenzo-furans (PCDFs), pesticides and heavy metals like mercury, lead, arsenic, cadmium and chromium

DICTIONARY

Quantitative data are data about numeric variables (e.g. how many; how much; or how often).

Qualitative data are measures of 'types' and may be represented by a name, symbol, or a number code

POPs are one of the major categories of PBTs which cause toxic effects on both humans and animals.

Similarly, heavy metals can also cause detrimental effects on both flora and fauna. They also bio-accumulate and bio-magnify along the trophic levels in food webs which exist in the ecosystem. Heavy metals persist in the environment for a long period of time, by having relatively high half-lives.

Therefore, qualitative and quantitative determination of the PBT levels in the environmental matrices as well in the animal bodies is important. This chapter focuses on the collection of environment and animal samples for analysis, sample transportation and labelling, sample extraction and separation, safety measures that should be followed during sampling and laboratory analysis and the safe disposal of the analyzed samples.

DICTIONARY

Environmental Matrices: something within or from which something else originates, develops, or takes form

With the advent of new technology, the power of analytics has progressed up to the level that we have the capability to measure in parts per trillion, instead of the usual ppm or ppb. Even in fundamental physical quantities such as length or mass, the units of femtoliters, femtometers or even attometers which describe the dimensions of individual atoms (10^{-18}) have been already achieved, albeit with high costs of analysis.

Overview

- General aspects
- Sample collection
    - Collection of samples from environmental matrices
        I. Air
        II. Water
        III. Soil
    - Collection of samples from animal bodies
        I. Blood
        II. Milk
        III. Tissues for histopathology
- Labelling and transportation
- Sample Extraction
- Sample Separation
- Analysis
    I. Qualitative analysis
    II. Quantitative analysis
- Safety precautions in sample collection and analysis
- Safe disposal of analyzed samples

5.1 General Aspects

The main category of PBTs that should be analyzed are Persistent Organic Pollutants (POPs). This category consists of organochlorine pesticides, industrial pollutants like PCBs and unintentional by-products like dioxins, furans and PAHs. Heavy metals are also an important category of PBTs. All these forms of PBTs are dispersed in different environmental matrices in diverse chemical forms. PBTs which are dispersed in air, water and soil are capable of causing adverse effects on living beings. Thus, the sampling, handling and qualitative and quantitative analysis of PBTs are important in order to investigate whether the levels of PBTs in these environmental matrices exceed the maximum permissible levels introduced by local and international authorities like World Health Organization (WHO), United States Environmental Protection Agency (US EPA) and Central Environmental Authority (CEA).

5.2 Sample Collection

It is a fundamental principle in any laboratory procedure, *that if the specimens have not been subjected to proper collection, labelling, handling or storage prior to and during the testing process it can be considered that* ***the value of the test is compromised or even become negated.*** If a sufficient number of samples are not collected or if standard procedures are not followed during sampling, the error reported with the final result might be considerably high, paving the way for wrong interpretation of data.

5.2.1 Air Sampling

Air sampling is an important aspect in POP analysis, since the majority of POPs are created in air and exist there. For instance, unintentional by-products of open burning like PAHs, dioxins and furans exist in air. However, air sampling is considered to be a relatively difficult sampling method compared to the other two sampling types; water sampling and soil sampling. There are some limitations of air sampling, there are only a limited number of monitoring stations that can be sited and monitored. Owing to this, in some occasions, representative samples cannot be obtained. Two sampling procedures are utilized in sampling gaseous PBTs which are namely,

1. Active sampling and 2. Passive sampling.

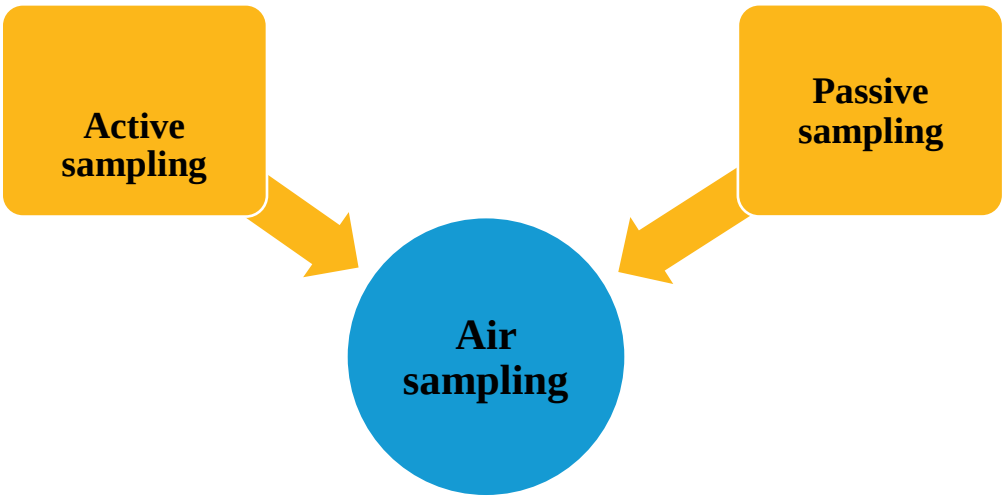


Fig. 5.1 Types of air sampling

The difference between active sampling and passive sampling

In active monitoring, a microbial air sampler *(shown below)* is used to force air into, or onto its collection medium



In passive monitoring, settle plates (Petri dishes) are opened and exposed to the air for specified periods of time to determine what microbiological particles may be present in the environment, as they may settle out of the ambient air, and onto the media surface



Active Sampling

Both air sampling procedures are normally occupied for sampling gaseous Persistent Organic Pollutants. Cumulative sampling is performed using active high-volume sampling with a rate of 0.5–1 m^3 per min. Active sampling can be considered as a conventionally used air sampling method currently employed in monitoring programs (Xu,Wang and Cai; 2013). E.g.: USEPA-method TO-9A for the analysis of PCDD/PCDFs in ambient air uses a high-volume air sampler equipped with a quartz-fibre filter and a Polyurethane Foam (PUF) adsorbent contained in a glass cartridge in order for sampling 325–400 m^3 air (Pozo *et al*; 2006). The European and Japanese standard methods for the stationary source and environmental monitoring of dioxins and DL-PCBs apply similar active sampling procedures (Grids; 2009).

5.2.1.1 Passive Sampling

Passive air sampling, due to its simplicity and economic advantages has achieved significant progress in the past fifteen years. This sampling method utilizes a sorbent with an appropriate capacity for Persistent Organic Pollutants, such as Polyurethane Foam and styrene/divinylbenzene co-polymer resin (e.g. XAD-2). For PUF-disk samplers, a three-month sampling period uses roughly 270–360 m^3 of air volume, which may be adequate for the detection of POPs (Pozo *et al*; 2006). XAD-based samplers are commonly deployed for longer time samplings (typically a year) (Shoeib and Harner; 2002). However, passive sampling can be considered as an economic, user friendly and feasible technique.

5.2.2 Water Sampling

A remarkable threat has been monitored in the aquatic life due to the addition of POPs used in agriculture and industries, into water ways including rivers, lakes, streams, and oceans etc. which have not been subjected to adequate treatment. Upon examination of the complex mixtures of chemicals present in natural water samples, the presence of organic chemicals was observed (Richardson and Ternes; 2011). *The chemical nature, chemical stability and solubility are some of the factors which determine the distribution of POPs in natural water bodies*. Therefore, it is important to analyze the POP levels in the aquatic environments, therefore for the analysis, sampling is an important aspect.

5.2.2.1 Precautions Followed During Water Sampling

There are some precautions that should be followed prior to water sampling;

- Refrain from using plastic materials as they may act as adsorption surfaces of the target compounds.
- It is recommended to store samples of POP-containing liquids in wide-mouth glass jars with PTFE (Polytetrafluoroethylene) caps.



Fig. 5.2 Wide mouth glass jars with PTFE caps

- Bottles in which Sampling is done should be washed with detergent, water and afterwards with organic solvents such as acetone, hexane or pentane before use.
- Highly lipophilic compounds such as four to six-ring containing aromatic hydrocarbon molecules or DDT and higher chlorinated PCB congeners have the risk of adsorption onto the container walls. Therefore, water samples shouldn't be stored for more than 2 hours and should not be moved into further containers before extraction.
- Representative samples from the original environmental matrix should be obtained
- When sampling is carried out for heavy metal analysis, acid-washed polyethylene bottles should be used.

5.2.2.2 Sampling Techniques

A spot (or grab) sample is defined as a discrete sample taken randomly (with regard to time and/or location) from the environment.
(https://www.mpdc.govt.nz/component/content/article/58-council-documents/policies-a-bylaws/1595-trade-waste-73?Itemid=647)

Standard scientific procedures should be followed during sample collection. The customary method for the collection of surface water samples is by grab or spot samples. This may involve taking a single sample or a composite sample representative of an integrated profile of width and depth. Collecting samples by hands is the convenient method when collecting samples from small streams while samplers should be utilized when collecting samples from deep water bodies.

A composite sample is defined as two or more samples or sub-samples, mixed together in appropriate known proportions (either discretely or continuously), from which the average result of a desired characteristic may be obtained

Existing supply wells or monitoring wells are the usual collection source for groundwater samples. The sampling methods vary depending on water depth and well size (Richardson and Ternes; 2011).

Time integrated or passive sampling techniques are employed to collect water samples for the analysis of POPs. Number of samples have been developed for the analysis of pollutants in water. These samplers include

- Semi permeable membrane device (SPMD)
- Polar organic chemical integrative sampler (POCIS)
- Chemcatchers
- polyethylene strips
- polymers on glass
- solid-phase microextraction (SPME) devices

SPMD and POCIS are most common samplers for the collection of water surface water samples. For instance, SPMD can be used to detect PCDD/PCDFs, PCBs and PAHs in aquatic environments.

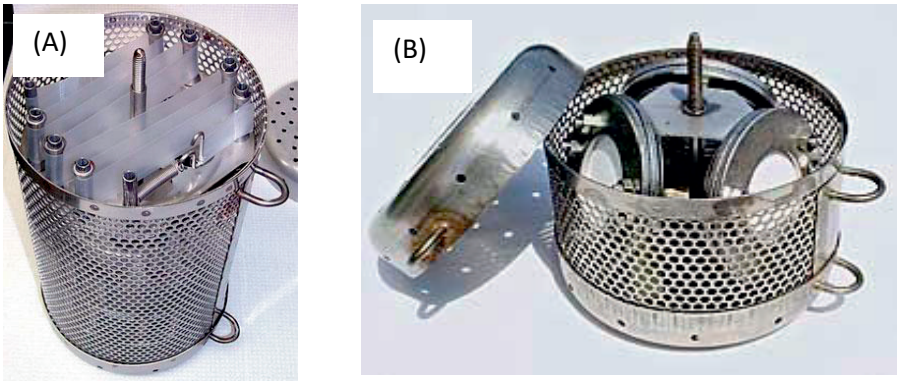


Fig. 5.3 (A) Semi permeable membrane device (SPMD), (B) Polar organic chemical integrative sampler (POCIS)

5.2.3 Soil Sampling

Soil has been identified as one of the major mediums for the accumulation of POPs as well as for the uptake by plants. Physio-chemical chemical properties of soil and sediments, especially the chemistry of organic carbon in the soil plays a vital role in absorption, accumulation and plant uptake of POPs from soil. Therefore, analysis of soil samples for different types of POPs is also important due to the adverse effects caused by these POPs in soil.

5.2.3.1 Soil Sampling Methodology

Sample collection should be performed as at locations as individual grab soil samples. It is recommended that these are selected and equally spaced. However since there may be differences in physical soil qualities (such as staining) the preferential selection of a sub-set of sampling locations may be necessary.

A stainless steel trowel or shovel should be used to collect soil samples, and should be from the top 10 cm depth (surface soils). They will be placed into a stainless-steel tray and stirred to result in a homogenous mixture. Afterwards samples will be put into one or more 125 ml or 250 ml glass jars.

5.2.3.2 Sampling Procedure

Precautions that should be followed prior to sampling;

- All sampling equipment such as dredge, mixing tray, spoon, should be thoroughly washed with metals-free soap and de-ionized water prior to sampling to prevent contamination.

Non-polar chemical solvents such as hexane and acetone should be used to ensure all residues and impurities are removed from the surfaces of equipment.



Collecting samples using stainless steel core sampler, trowel or shovel.

Collect five sub-samples between 1 and 20cm below surface from area 1m x 1m.



Stir to a homogenous mixture



Place samples in glass jars

Source:

http://www.popstoolkit.com/sops/methods/soil.aspx

5.2.4 Sample Collection from Animal Bodies

Not only the environmental matrices, but also the living organisms also can be accessible to POPs. Thus, special scientific procedures also should be carried out for biological sample collection. Recent studies seriously emphasize that breast milk and blood are more prone to POP contamination. However, ensuring ethical clearance is a vital aspect in biological sampling as it may otherwise create controversies in the society.

POP Sampling in Breast Milk

Human breast milk is the best food for infants, which is comprised of all nutrients required by infants. Human milk is a relevant matrix for determination of body POP burden (UNEP 2007). The target group for sample collection will be desired based on research and following standard procedures should be followed during sampling.

- The use of composite samples is recommended to determine the concentrations of dioxin-like PCDDs, PCDFs and PCBs in human breast milk and individual samples to determine basic POP pesticides and PCB markers (UNEP; 2010).
- Identification of volunteers, preferably women at 2 to 4 weeks' after childbirth (UNEP; 2007)
- Preparation of sampling materials and interviews
- Preparation of personal protective equipment for treating the breast milk as a bio-hazard
- Sealed sample jars are provided to mothers

5.2.4.1 POP Sampling in Human Blood

Human blood sampling is carried out in volunteer basis. The following selected groups of people will be subjected to blood sampling;

- Those who are suspected to be exposed to (PCB) contamination for at least four years (through dermal contact, ingestion, and/or inhalation);
- Those who fulfil the blood eligibility criteria
- Those who have given informed consent. (POPs toolkit)

- A target volume of 80 mL is obtained from each donor.
- Blood samples will be kept cool on ice packs during the sampling procedure to prevent microbial infection, and frozen within one hour of collection (4^0C).

5.2.5 Sample Collection for Heavy Metal Analysis

Samples for heavy metal analysis can be carried out using pre-cleaned acid-washed polyethylene containers. Representative samples can be obtained either by collecting grab samples or composite samples. Water samples should be acidified using concentrated HNO_3 upon collection and stored in 4^0C until the analysis is carried out. Further, the soil and sediments should be digested according to standard analytical procedures prior to analysis.

5.3 Sample Labelling, Transportation and Storage

Proper labelling, transportation and storage of the collected samples, play an important role in PBT analysis since it directly affects the final outcome of the analysis. Thus, proper scientific procedures also needed to be followed during these three stages.

Every container carrying wastes containing or contaminated with PCDD, PCDF, HCB (Hexachlorobenzene) or PCB should be clearly labelled with a hazard-warning label and a label providing details of the container. Such details should include the contents of the container (exact weight or volume of a liquid, type of waste carried).

Sampling date and time, address (GPS), equipment and sampling serial number, operator's name and reference are some significant facts that should be given in the labels of the bottles containing the samples. Storing samples in a cold place at low temperature and maintaining a chain of custody of the samples are also required.

Apart from labelling, some regulations are also applicable when transporting and storing hazardous material containing POPs. These include, handling by trained operators, transporting only by licensed carriers, storing in secure premises away from sensitive areas (such as wetlands and food preparation sites) and under conditions (impervious floor, bund walls to contain spills) which prevent off-site migration.

5.4 Sample Preparation for Analysis

Samples collected according to the scientific procedures, should be prepared for the qualitative and quantitative analysis by extracting and separating the intended material from interfering compounds so that the errors do not affect the final outcome of the analysis. The extraction and separation methods also depend on the targeted analytical technique.

5.4.1 Sample Extraction

Samples from different environmental matrices including;

- Soil
- Water
- Sludge
- Polyurethane foam and resins
- Plant animal tissues

Should be extracted so that the further analysis can be carried out.

Following extraction procedures are followed when extracting POPs for the laboratory analysis.

- **Accelerated Solvent Extraction (ASE)**

Accelerated Solvent Extraction system is used for the extraction of compounds from solid and semi-solid samples in less time with small solvent volumes. Elevated temperatures and pressures accelerate the extraction process. This method saves time, solvent, and money, and generates results in very quickly compared to traditional techniques such as Soxhlet or sonication.



Fig. 5.4 ASE system

- **Soxhlet extraction**

Soxhlet extraction is used when the desired compound has a limited solubility in a solvent, and is insoluble in that particular solvent. It uses efficient recycling of a small amount of solvent to dissolve a larger amount of material.

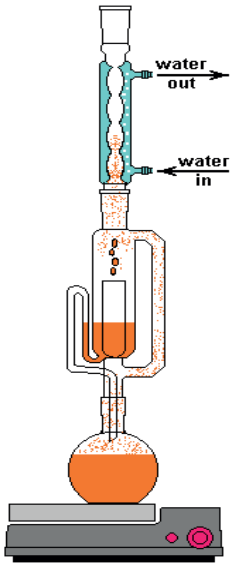


Fig. 5.5 Soxhlet extraction apparatus

- **Sonication**

Sonication is the application of sound energy to agitate samples. Ultrasonic frequencies (> 20 kHz) are used. This method is used for the extraction of biological samples by disrupting the cell walls.



Fig. 5.6 Sonication apparatus

- **Solid Phase Micro Extraction (SPME)**

This technique that involves the use of a fibre coated with an extracting phase, this phase could be a liquid (polymer) or a solid (sorbent) which are capable of extracting different kinds of analytes (including both volatile and non-volatile) from different media, such as liquid or gas phase. The quantity of analyte extracted increases when its concentration in the sample increases.

DICTIONARY

Sorbent: a substance which has the property of collecting molecules of another substance by adsorption or absorption.

- **QuEChERS (Quick, Easy, Cheap, Effective, Rugged, Safe)**

This method is readily used for pesticide residue analysis. This is a type of dispersive solid phase extraction (dSPE) developed to extract pesticide residues with a relatively polar acetonitrile compounds in food and agricultural samples. Now this has been extended to analyze other chemical classes.

Table 5.1: Extraction conditions for different categories of POPs (US EPA method 3545)

Conditions	Pesticides	HCB	PCB	PCDD/F
Temperature	100 ^{0}C	100 ^{0}C	100 ^{0}C	175-200 ^{0}C
Pressure	1.0342×10^7 Pa	1.0342×10^7 Pa	1.0342×10^7 Pa	1.0342×10^7 Pa
Time	12 min	12 min	12 min	22 min
Solvent	Hexane/ Acetone	DCM/ Acetone	Hexane/ Acetone	Toluene

5.4.2 Sample Separation

Sample separation is carried out in order to eliminate the synergistic effect of some elements like sulphur on the final outcome. The first step is using concentrated sulfuric acid or gel permeation chromatography (GPC) to remove lipids. Elemental sulphur is another interfering substance that commonly occurs in sediment, sewage and sludge. Sulphur is removed using activated copper or tetrabutylammonium sulphite mixed with the extract or mounted on the top of the silica column, Multi-layer adsorption columns, with different combinations of neutral/acidic/basic silica, alumina, Florisil and active carbon are mostly utilized to remove

co-extracted pigments, low molecular-weight lipids and other interfering materials (Spinnel *et al*; 2008).

DICTIONARY

Synergistic Effect: An effect arising between two or more agents, entities, factors, or substances that produces an effect greater than the sum of their individual effects

5.5 Analysis

Analysis of PBTs can be done either qualitatively or qualitatively. As explained at the beginning of the chapter, qualitative analysis indicates the presence of a particular compound or an element in a sample while quantitative analysis indicates the exact amount of the tested pollutant. Moreover, through quantitative analysis it can be determined whether the pollutant of interest exceeds the maximum permissible level (MPL) so that it can exert adverse effects on living beings.

5.5.1 Qualitative Analysis

After the purification and separation of the targeted samples, qualitative analysis can be performed in order to identify the basic chemical and physical properties of the samples. Since most of the POPs are chlorinated organic compounds, basic experiments can be carried out for the qualitative identification.

Qualitative analysis includes,

- Measuring the boiling or melting point
- Measuring the solubility
- If the compound is water soluble, the pH can be measured
- The presence of aromatic rings (eg: PAHs) can be tested with Aluminum chloride and chloroform
- Flame test to identify the presence of metallic elements including heavy metals.

5.5.2 Quantitative Analysis

Diverse analytical techniques can be employed for the quantitative analysis of POPs. Some of these techniques are,

- **Gas chromatography**

GC is the commonly used analytical technique for the quantitative determination of POP levels in the environmental matrices and in animal bodies.

Table 5.2 summarizes the GC analytical methods which can be utilized to determine the POPs in environmental matrices and animal bodies.

DICTIONARY

Elution: the process of extracting one material from another

Table 5.2: GC methods for the quantitative determination of POPs (Xu,Wang and Cai; 2013)

Compound class	Analytical method
Chlorobenzene	GC-ECD
PCBs (total)	GC-ECD
OC pesticides	GC-ECD
PAHs	GC/MS
PCBs (dioxin like)	GC/MS GC/HRMS
Dioxins furans	GC/MS GC/HRMS

GC- Gas Chromatography ECD- Electron Capture Detector, MS- Mass Spectroscopy, HRMS High Resolution Mass Spectroscopy

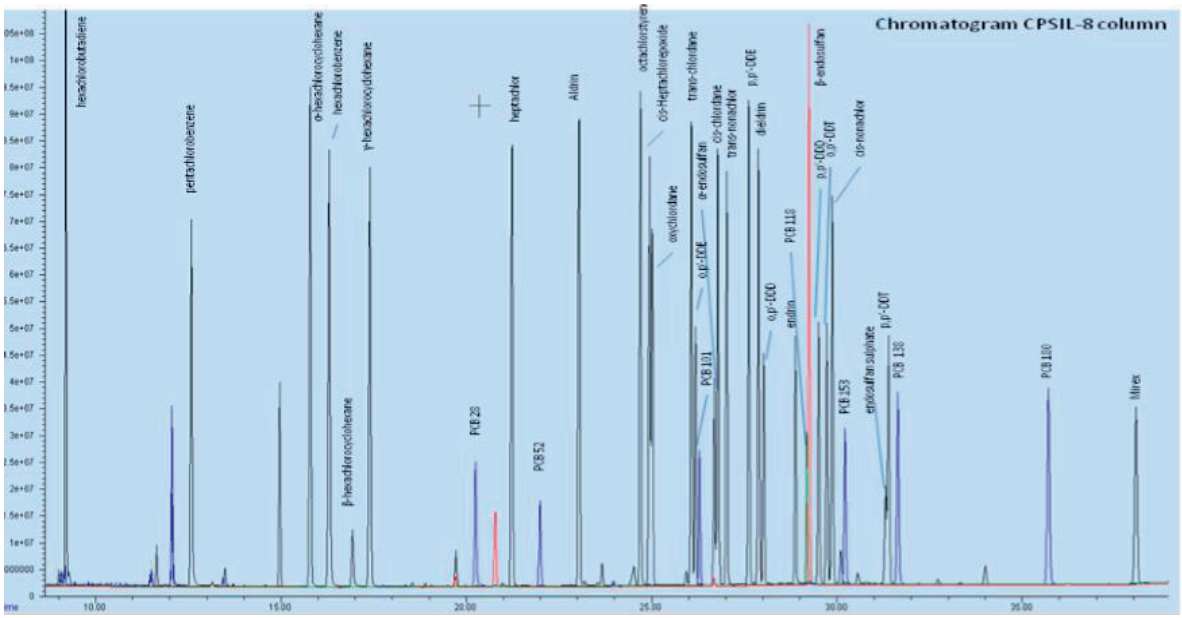


Fig. 5.7 Example for a chromatogram obtained for a mixture of POPs

When the analysis is carried out using the GC,

- Suitable temperature programme should be selected in order to prevent the general elution problem (increasing the retention factor so that the resolution is increased)
- Inert carrier gas like He, N_2 can be used.
- Injection temperature should be selected so that it is about 50^{o}C higher than the boiling point of the analyte.
- Qualitative identification also can be done by comparing the retention times of the standards with the analytes.

Quantitative determination can be carried out using the calibration curve method, where concentration is plotted against the peak area or peak height

Where,

$$\text{Peak area or peak height} \propto \text{Analyte concentration} \qquad (5.1)$$

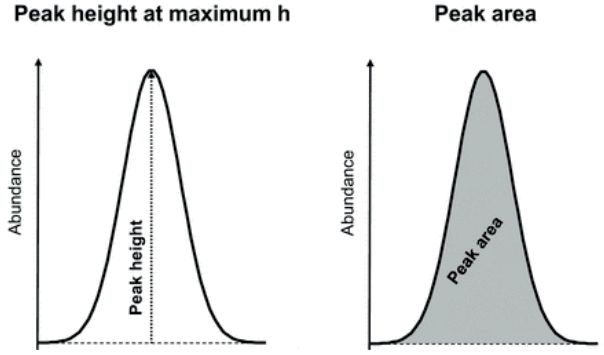


Fig. 5.8 Peak height and peak area (Adapted from Dettmer-Wilde, K., Engewald, W. (2014))

- **High Performance Liquid Chromatography (HPLC)**

HPLC delivers a pressurized liquid solvent which contains the sample mixture through a column containing a solid sorbent material. Sample components interact differently with the sorbent material paving the way for different flow rates and ultimately causing the separation into its components.

Isocratic and gradient elution techniques are employed to eradicate the general elution problem in HPLC. *(see explanation)*

Isocratic elution is defined as an elution where the *composition* of the analyte and the liquid used to dissolve the analyte (mobile phase) is constant.

Gradient elution is defined as an elution where the *composition* of the analyte and the liquid used to dissolve the analyte (mobile phase) is varied.

- **Thin Layer Chromatography**

This is used to separate non-volatile mixtures. Silica or aluminum oxide are used as sorbent material and this is known as the stationary phase. According to the polarity of the analyte, their affinity to the mobile phase solvent varies. Quantitative analysis can be done by calculating and comparing the retention factor (R_f)

$$Retention\ factor\ (R_f) = \frac{Distance\ travelled\ by\ the\ analyte}{Distance\ travelled\ by\ the\ solvent\ front} \qquad (5.2)$$

- **Column chromatography**

In column chromatography, an adsorbent is packed inside the column and solvent is poured at the top. The separation of the analyte depends on its affinity to the mobile phase.

Analytical methods which can be used to detect other PBTs (Heavy metals)

Among the numerous analytical methods employed for the quantitative analysis of heavy metals, Atomic Absorption Spectroscopy can be named as the most widely used analytical method. Other methods are, Ion chromatography, X-ray fluorescence spectroscopy and anodic stripping voltammetry.

- **Atomic Absorption Spectroscopy (AAS)**

In AAS, an external source of radiation impinges on the analyte vapour. If the radiation is of the appropriate frequency, it is absorbed by the analyte atoms and promote to the excited state. Within a few nano-seconds, the excited atoms descend to the ground state by transferring excess energy to the other atoms.

Quantitative analysis can be done by constructing a calibration curve according to the Beer Lambert law.

Beer Lambert law can be expressed as;

$$A = \in . C . l \qquad (5.3)$$

Where, A is the absorbance, ∈ is the molar absorption coefficient, C is the concentration of the analyte and l is the path length. According to this equation, *A* is proportional to *C*.

- **Atomic Emission Spectrometry (AES)**

During AES analysis, intensity of light emitted from a flame, plasma, arc or spark at a particular wave length is used for the quantitative determination of the elements.

- **Inductively Coupled Plasma Mass Spectrometry (ICP MS)**

An ICP-MS is a combination of a high-temperature Inductively Coupled Plasma (ICP) source with a mass spectrometer. The ICP source ionizes the elemental atoms in the sample. These ions are then separated and detected by the mass spectrometer.

- **Ion Chromatography (IC)**

Ion chromatography is a form of liquid chromatography, which provides a quantitative measure of ions by comparing their bonds with a resin. Ionic species differentiate themselves according to ion type and size. The mixture runs through a pressurized chromatographic column where ions are adsorbed by constituents in the column. An ion extraction liquid, known as the *eluent*, runs through the column, the adsorbed ions begin separating from the column. The retention time of different species determines the qualitative ionic characteristics in the sample.

- **X ray Fluorescence Spectroscopy (XRF)**

X-ray fluorescence (XRF) spectrometry is an elemental analysis technique broadly used in science and industries. XRF is based on the principle that individual atoms upon excitation by an external source of energy, emit X-ray photons of a characteristic unique energy or wavelength. Upon observation of the type of wavelength and the number of photons emitted by each wavelength from a sample, the elements present may be qualitatively and quantitatively identified.

- **Anodic Stripping Voltammetry (ASV)**

ASV is utilized to determine trace levels of metal contaminations. It involves electroplating a metal by reduction onto an electrode (deposition step) from an original solution and reoxidizing the metal back into another solution (stripping step). The reduced metal following the deposition step has a concentration usually 100 – 1000 times higher the original solution concentration. The time for deposition ranges from 30 seconds for solutions containing metal

ions at concentrations on the order of 10^{-7} M while the time increases for more than 20 minutes for those down to 10^{-10} to 10^{-11} M. The electric potential at the stripping step is called the stripping response and used to identify the metal. Standard solutions containing known concentrations of each metal are used to calibrate the stripping response which is used for comparison with unknown metals. The magnitude of the current (peak height) or charge (peak area) of the anodic wave may be used to identify unknown amounts of analyte.

5.6 Health and Safety Considerations

Due to the bio accumulative, mutagenic and carcinogenic nature of POPs, it is essential to follow several precautions during sample collection and analysis of these compounds.

- Helmet, disposable suit, goggles and proper chemical resistant gloves should be used during sampling and transportation. In addition, protective shoes, respiratory mask, goggles and a protective suit also can be employed.



Fig 5.9 Personal Protective Equipment

This equipment is collectively called Personal Protective Equipment (PPE).



Fig. 5.10 Illustrations of PPE

- Analysis should be carried out in laboratories where good ventilation conditions are provided.
- For laboratory work, laboratory coats and suitable disposable gloves are essential for protection against chemicals contacting with skin. If there is a hazard of formation of dust or fume (for example from heating), a fume cupboard is advised for usage.
- Regular cleaning and maintenance of instruments are essential



Fig. 5.11 Disposable lab coat and gloves



Fig. 5.12 Use of fume cupboard

5.7 Safe Disposal of Analyzed Samples

Various methods can be employed to destroy the POPs which are used in analyzing purposes.

Traditional methods of destruction of POPs involve land filling, ground storage, deep well injection, combustion by open burning, incineration in cement kilns or metal furnaces. But there are limitations in the incineration process like the unintended production of chemicals like dioxins, PCBs and HCBs in higher amounts and this also induce adverse effects on the workers and local population.

PCBs are difficult to destroy since they contain chlorines. They produce toxic dioxins during combustion. Similarly, the destruction of HCBs and Mirex is also difficult.

Combustion:

This method of disposal is the most common one but it is not considered as an environmentally sound technique. PCBs undergo pyrolysis to water, carbon dioxide and hydrogen chloride (HCl) when burnt at temperatures 1400-1600^{o}C. This method has potential dangers of producing highly hazardous chemicals which are toxic and can cause significant effects on living organisms. This risk has a higher probability when the combustion temperature is lower than 1200^{o}C.

DICTIONARY

Pyrolysis: the decomposition of chemical compounds due to high temperatures.

Encapsulation / burial:

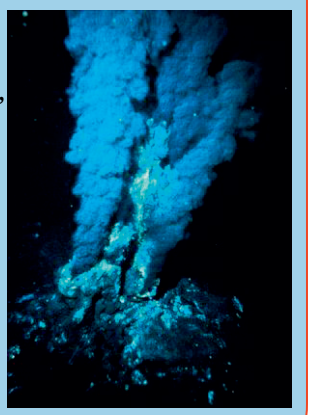
Though this method is not a destruction method, it can effectively seal the material and avoid the pollution of this compound for long periods. Concrete capsules can be made and used to bury the POPs and seal them off by concrete. Once this is done, when the concrete loses its capacity after an extremely long time, it may allow leakage of POP material causing it to finally reach out and contaminate the water resources.

Chemical treatment of PCB's with Sodium Hydroxide:

The method has been attempted for the destruction of PCBs. In this method, sodium hydroxide is made to react with PCBs to generate sodium chloride with biphenyl and phenolic mixtures being generated as side by-products. Though the technique appears to be simpler, the method has not acquired popularity as the side products of the reaction are phenols and have a higher solubility with water and therefore has an easy mode of spreading the toxic material by travelling in aqueous systems for long distances. This situation can be very threatening as it can cause much higher damage immediately as compared to PCBs themselves.

Super Critical Water oxidation of PCB's: Super critical conditions can be achieved for any material in which liquid and vapor states co-exist and are not distinguishable. Water achieves this condition when its temperature is above 374°C and pressure at 221 bar. At this condition, water is called Super-Critical water and is used in the destruction of hazardous waste. PCBs, PAHs, waste plastics and other materials can be converted in to simple hydrocarbons which can be reused and recycled. The technology is not yet perfected and needs a lot of technological development to meet the requirements of PCB destruction.

Do you know? : Supercritical water is found in nature. Deep down at the very bottom of the Atlantic Ocean, geochemist Andrea Koschinsky has found something truly extraordinary: "It's water," she says, "but not as we know it."
At over 3 kilometres beneath the surface, sitting atop what could be a huge bubble of magma, it's the hottest water ever found on Earth. The fluid is in a "supercritical" state that has never before been seen in nature.
The fluid spews out of two black smokers called *Two Boats* and *Sisters Peak*. Koschinsky, from Jacobs University in Bremen, Germany, says it is somewhere between a gas and a liquid. She thinks it could offer a first glimpse at how essential minerals and nutrients like gold, copper and iron are leached out of the entrails of the Earth and released into the oceans. Liquids boil and evaporate as temperature and pressure rise. But push both factors beyond a critical point and something odd happens: the gas and liquid phase merge into one supercritical fluid. For water, this fluid is denser than vapour, but lighter than liquid water.



Source:https://www.newscientist.com/article/dn14456-found-the-hottest-water-on-earth/

Sodium metal-based conversion of PCB's:

In this process, sodium metal reacts with the chlorinated systems to dechlorinate the molecules at much lower temperatures than combustion.

5.8 Global Monitoring Plan on Persistent Organic Pollutants

The Stockholm Convention on Persistent Organic Pollutants has been established with the purpose of protecting human health and the environment from POPs. Elimination of the production, use and emission of POPs are some of the aims of this international agreement. (https://ipen.org) Under the auspices of the Stockholm Convention, the parties proposed a mechanism to evaluate whether the objectives of the convention were achieved. According to Article 16 of the Convention, its effectiveness shall be evaluated starting four years after the

date of entry into force of the Convention and periodically thereafter at intervals to be decided by the Conference of the Parties. The 22 POPs covered under the Convention are covered and it provides a coordinated network of measurement data in air, human milk and blood and other media.

A guidance document related to the Global Monitoring plan was formulated by the parties (UNEP 2015 available at http://www.pops-gmp.org/res/file/UNEP-POPS-COP_7-INF-39_English.pdf). For example, with regard to air sampling, the sampling window for the initial baseline is 2003, plus or minus five years. Sample frequency and timing should, as much as possible, be harmonized between matrices. To satisfy that requirement, the samples should be taken at least annually and during the same period in every year. For some matrices where seasonal influences would be less important (e.g. human breast milk), the sampling frequency and duration might be different. For the statistical analysis of the levels it would be preferable to take many samples frequently from one location rather than to take a few samples from many different locations.

The first edition of the guidance for the Global Monitoring Plan was developed and published in 2004, by UNEP Chemicals. Further to the second meeting of the Conference of the Parties to the Stockholm Convention, a Technical Working Group (TWG) was mandated to revise the original guidance document, in order to provide comprehensive technical guidance on all aspects of the implementation of the Global Monitoring Plan, including issues related to statistics, sampling, sample preparation, analytical methodology and data management.

5.8.1 Quality Assurance in the Global Monitoring Programme

A critical aspect for any air monitoring program is to implement and document a quality assurance and quality control (QA/QC) program. This is key to ensuring the credibility of the data and that it can be used to establish long-term trends and that it can be evaluated in terms of its comparability with results from other programs and sampling approaches.

Inter-laboratory exercises are often used to assess the effectiveness of QA/QC practices among several participating labs and to provide a measure of interlab comparability. This usually involves the circulation and analysis of a common standard or reference sample, often at two or more concentration levels. Recent international inter-laboratory studies for POPs with a focus on air have been conducted through AMAP/EMEP/NCP (Schlabach et al., 2012). Some quality assurance approaches are cited below from Weber et al 2017.

- cleaned laboratory equipment, material, and chemicals to be used to avoid contamination from background;
- system ensuring that effectiveness of the measurements and procedures is continuously supervised through the analysis of procedural blank samples;
- regular injection of solvent blanks and standard solutions;
- tests to be carried out to evaluate the accuracy of the method, e.g. efficiency of the extraction methods, the recovery of the analytes, stability and loss of analytes in solution during storage, calibration using matrix matched standards or standard addition, and use of proper internal standards;
- tests to be carried out to evaluate the precision (repeatability and reproducibility), the limits of detection (LODs) and quantification (LOQs), the robustness and the specificity of the whole method, from sampling to detection;
- clearly defined criteria for identification and quantification need to be applied, and calibration curves to be used;
- Storage of analyzed samples and data (including instrumental raw data) for a defined time.

5.9 Monitoring of PBTs in Products

POPs are used in articles and products are also included in larger re-use and recycling flows (e.g. used electrical and electronic equipment (EEE), waste electrical and electronic equipment WEEE and related plastics for recycling, second hand vehicles, polyurethane foams, synthetic carpets, certain furniture, textiles, recycled wood and paper). A reason to screen and analyze POPs in articles and products is their relevance for human exposure. POPs in articles and products are closely linked to human exposure. While for legacy POPs the major exposure is with food, a major exposure for industrial POPs come from products. For PBDE a major exposure stem from chemicals in consumer goods like furniture, vehicles or specific polyurethane (PUR) foam products. Also toys even from recycling of PBDE containing articles can lead to relevant exposure of children. Also the recycling of PBDE containing PUR foam resulted in high blood levels in recyclers and carpet installers (Weber et al 2017). It is important to screen products and articles for POPs since the Global Monitoring Plan does not sample industrial products.

6 Control and Management

6.1 General Introduction to Control and Management

PBTs are toxic chemicals that have the ability to travel extensive distances through air and water, and undergo accumulation in the fat of living beings. They don't break down rapidly with time and can have the potential to expose people to various health issues including birth defects, cancer, immunity defects, brain damage and nervous system impairments. Many PBTs have their widespread applications in pest and disease control in agriculture and several industrial processes for specific uses. Other PBTs are produced as unintentional by-products from the above applications, such as waste material incineration and in the manufacture of chlorinated chemicals.



Fig. 6.1 Open burning of waste at unregulated dumpsites (Adapted from: SPREP, 2015)

In Sri Lanka the biggest source of unintentional by-products comes from waste incineration which is mainly of medical wastes and open burning processes at the domestic scale. Figure 6.1 is a photo taken at a waste burning open dumpsite which clearly shows the associated adverse effects in the environment and human health. So several decades ago, various organizations, conventions and authorities have come forward to eliminate or reduce the impacts of PBTs globally and nationally.

Such conventions are the Stockholm Convention, Basel Convention and Rotterdam Convention which addresses the matter of persistent bio-accumulative toxic chemicals at a global scale. Being a signatory country of the Stockholm Convention, Sri Lanka has also ratified some rules and regulations of the convention based on a NIP (National Implementation Plan). Therefore, Sri Lanka has also enacted several legislations for eliminating or reducing the production, use and/or release of these pollutants such as the Control of Pesticides Act, No. 33 of 1980 (Amendment Act No.6 of 1994).

Reducing the risks of PBTs is not a simple target and should be achieved gradually using preventive measures such as promoting shifts to alternatives (chemical and non-chemical). PBT alternatives can be encouraged through awareness campaigns, economic incentives, voluntary programs and constructing rules and regulations for enhancing the use of alternatives. In the meantime, appropriate punishments such as imprisonment and fines against users of PBTs should also enforced.

6.1.1 Pollution Prevention (P2)

Pollution prevention (P2***)*** *is any practice that reduces, eliminates, or prevents pollution at its source* and also known as 'source reduction' and facilitates waste management through a prevention approach. Reducing the amount of pollution produced means less waste to control, treat, or dispose of. Less pollution means less hazards posed to public health and the environment (US EPA).

Pollution Definition:

Pollution is defined as the contamination of the Earth and atmosphere to such an extent that normal environmental processes are adversely affected. Polluted elements are disagreeable, toxic, harmful and/or objectionable.

- Pollution may be natural, such as due to volcanic eruptions, as well as anthropogenic.
- It can be purposeful or it can be accidental.
- It includes the release of substances or energy which harm the sustainable quality of air, water and soil, and which reduces the human quality of life [Pearson Education Ltd; 2014].

Pollution can be of two major sources; point source or non-point source.

DICTIONARY

Point source pollution refers to discrete sources of contaminants (e.g. the nuclear explosion at Chernobyl, Ukraine and industrial pollution at Bhopal, India)

Non-point source pollution refers to more dispersed sources (e.g. air pollution from numerous widely dispersed origins like vehicles and industries).

Point-source pollution is usually more manageable. Due to localization of the point source, legal prosecution, emission control and apportion of responsibility is easier. Even the impact is manageable due to localization.

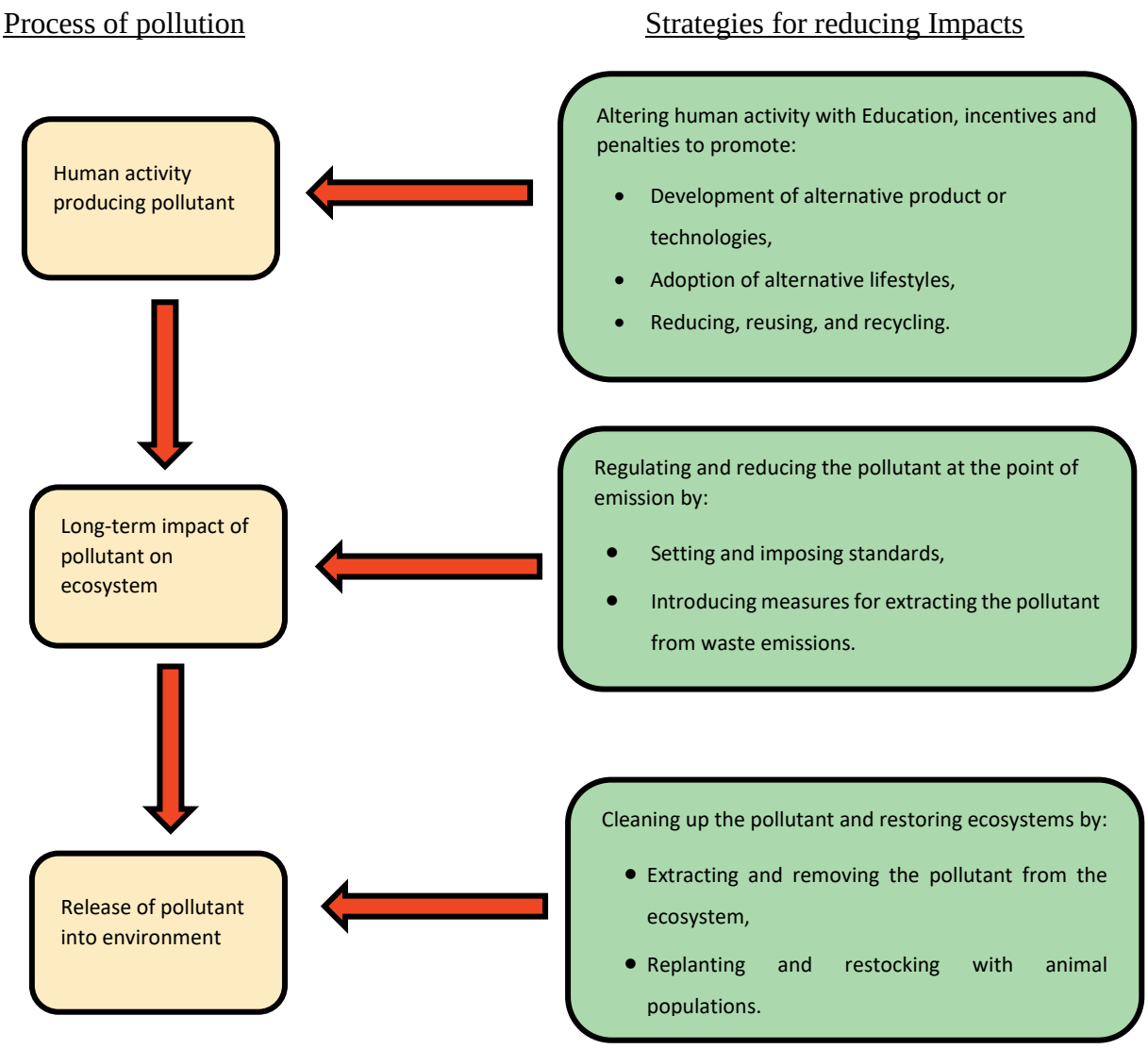


Fig. 6.2 Process of pollution and management strategies.

6.1.2 Green Chemistry and Green Engineering Principles

Most of the environmental and health risks of chemicals can be avoided if proper considerations are given to these aspects during the development and synthesis of new chemicals. Green chemistry principles provide chemists with guidance to develop less harmful chemicals. There are 12 principles of green chemistry and 12 principles of green engineering that can be applied at the product or process development stage to ensure proper consideration is given to environmental and health risks associated with the products and take appropriate decisions to reduce the risks, to improve the material and energy efficiency.

The twelve principles of green chemistry are:

1. **Prevention**. Preventing waste is better than treating or cleaning up waste after it is created.
2. **Atom economy**. Synthetic methods should try to maximize the incorporation of all materials used in the process into the final product. This means that less waste will be generated as a result.
3. **Less hazardous chemical syntheses**. Synthetic methods should avoid using or generating substances toxic to humans and/or the environment.
4. **Designing safer chemicals**. Chemical products should be designed to achieve their desired function while being as non-toxic as possible.
5. **Safer solvents and auxiliaries**. Auxiliary substances should be avoided wherever possible, and as non-hazardous as possible when they must be used.
6. **Design for energy efficiency**. Energy requirements should be minimized, and processes should be conducted at ambient temperature and pressure whenever possible.
7. **Use of renewable feedstocks**. Whenever it is practical to do so, renewable feedstocks or raw materials are preferable to non-renewable ones.
8. **Reduce derivatives**. Unnecessary generation of derivatives should be minimized or avoided if possible; such steps require additional reagents and may generate additional waste.
9. **Catalysis.** Catalytic reagents that can be used in small quantities to repeat a reaction are superior to stoichiometric reagents (ones that are consumed in a reaction).

10. **Design for degradation**. Chemical products should be designed so that they do not pollute the environment; when their function is complete, they should break down into non-harmful products.

11. **Real-time analysis for pollution prevention**. Analytical methodologies need to be further developed to permit real-time, in-process monitoring and control *before* hazardous substances form.

12. **Inherently safer chemistry for accident prevention**. Whenever possible, the substances in a process, and the forms of those substances, should be chosen to minimize risks such as explosions, fires, and accidental releases.

Twelve principles of green engineering:

1. **Inherent Rather Than Circumstantial** – Designers need to strive to ensure that all materials and energy inputs and outputs are as inherently nonhazardous as possible.

2. **Prevention Instead of Treatment** – It is better to prevent waste than to treat or clean up waste after it is formed.

3. **Design for Separation** – Separation and purification operations should be designed to minimize energy consumption and materials use.

4. **Maximize Efficiency** – Products, processes, and systems should be designed to maximize mass, energy, space, and time efficiency.

5. **Output-Pulled Versus Input-Pushed** – Products, processes, and systems should be "output pulled" rather than "input pushed" through the use of energy and materials.

6. **Conserve Complexity** – Embedded entropy and complexity must be viewed as an investment when making design choices on recycling, reuse, or beneficial disposition.

7. **Durability Rather Than Immortality** – Targeted durability, not immortality, should be a design goal.

8. **Meet Need, Minimize Excess** – Design for unnecessary capacity or capability (e.g., "one size fits all") solutions should be considered a design flaw.

9. **Minimize Material Diversity** – Material diversity in multicomponent products should be minimized to promote disassembly and value retention.

10. **Integrate Material and Energy Flows** – Design of products, processes, and systems must include integration and interconnectivity with available energy and materials flows.

11. **Design for Commercial "Afterlife"** – Products, processes, and systems should be designed for performance in a commercial "afterlife."

12. **Renewable Rather Than Depleting** – Material and energy inputs should be renewable rather than depleting

More information, visit https://www.acs.org/content/acs/en/greenchemistry.html

Atom Economy

This is a novel concept in green chemistry used to gauge how much product is wasted. It consist of a simple formula which wishes to calculate how much useful product in terms of atoms is produced at the end of a process.

The simple definition is stated as “the ratio between the mass of desired product to the total mass of products, expressed as a percentage”.

For example, if a process to produce a synthetic polymer produces 50g of the polymer and 50g of high weight waste products, the total weight of product is 100g, and the atom economy value is 50%.

6.2 Prioritization and Assessment Schemes

6.2.1 Proposed General Risk Assessment Scheme

Upon consideration of the great number of untested chemical constituents that currently exist, to which PBTs comprise a specific subdivision demanding international cooperative action, it would be applicable to form a reliable procedure of selection and assessment.

A possible plan for group prioritization of current chemicals is shown in Figure 6.3 below. Under such a plan, possible POPs or PBTs could be fast tracked for initial screening prior to a more expensive and lengthy, full-scale risk assessment. Initial selection criteria for PBTs would compose of the potential for long distance transport followed by persistence and bioaccumulative potential.

The stage of risk assessment will thereafter measure the actual or expected levels of environmental exposure to the substance *(exposure assessment)* and the likely significance of any resulting adverse effects *(effects assessment).*

It is of the greatest importance that, the type of effects assessment used, will be applicable for the group of chemicals concerned. In the case of suspected PBTs, this should include tests for the chronic effects (effects on immune system, endocrine effects, developmental, neural, behavioral effects and carcinogenicity).

When the levels of doubt involved in predicting exposure and the resultant effects on ecosystems (wildlife/humans) are high, expert decision and weight-of-evidence, based on the preventive principle, may have to be used to decide if the risks are acceptable.

This is common for new substances that would be released into the environment for which future production data, use and emission volumes are only predictions, and therefore exposure assessments are much more uncertain (Vallack et al; 1998).

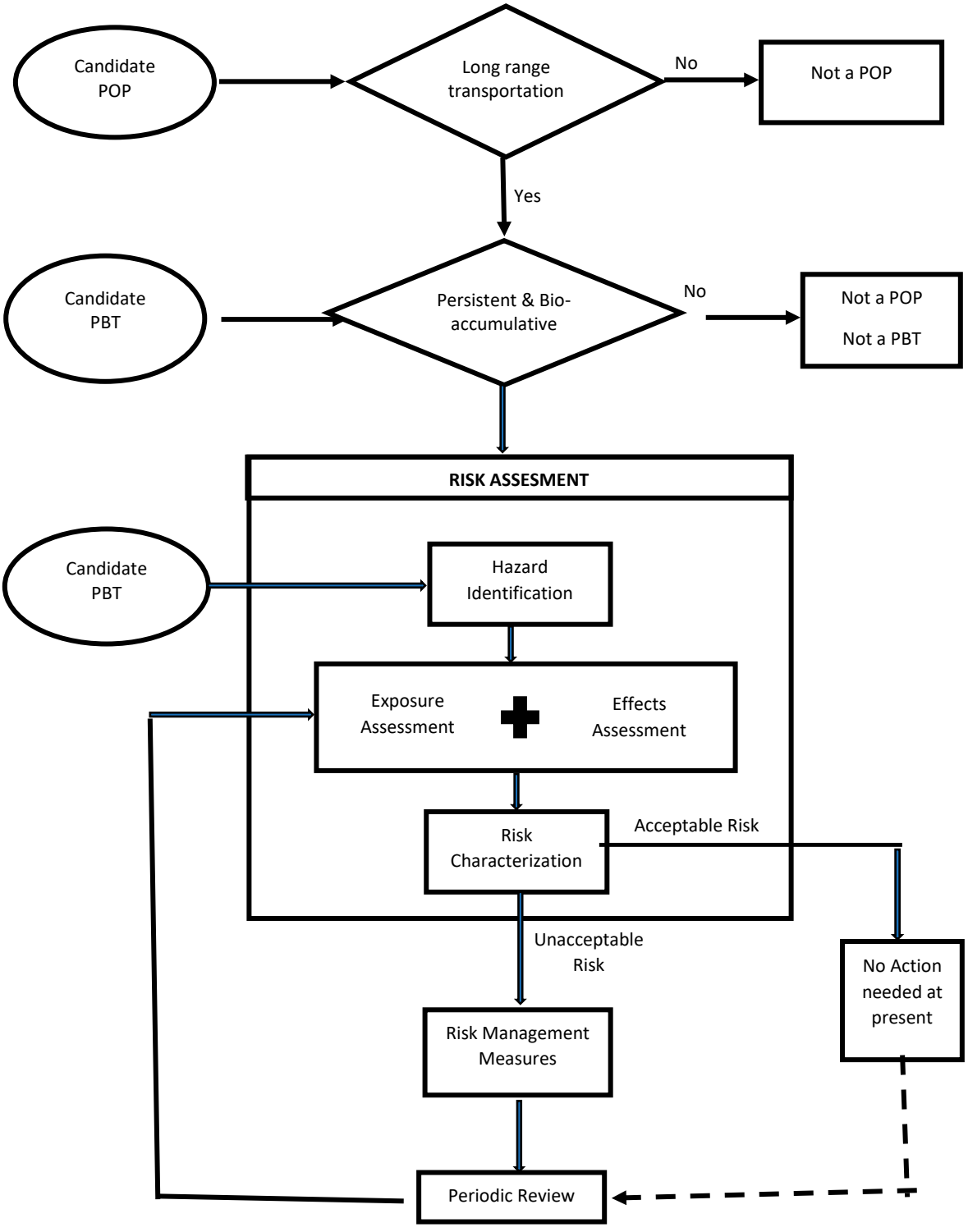


Fig. 6.3 Proposed general chemical risk assessment scheme.

6.3 Strategies for Controlling and Management of PBTs

The global use of materials is accelerating day by day. The return of substances back to the environment was raised by 26% from 1975 to 2000 and the quantity of materials currently in use (mainly as durable products, buildings and roads, or "net additions to stock") increased by 83%. On a historical basis, population, economic growth and new technologies have resulted in an increased use of materials, energy and water. So proper control and management of those materials, especially PBT chemicals is an essential process today.

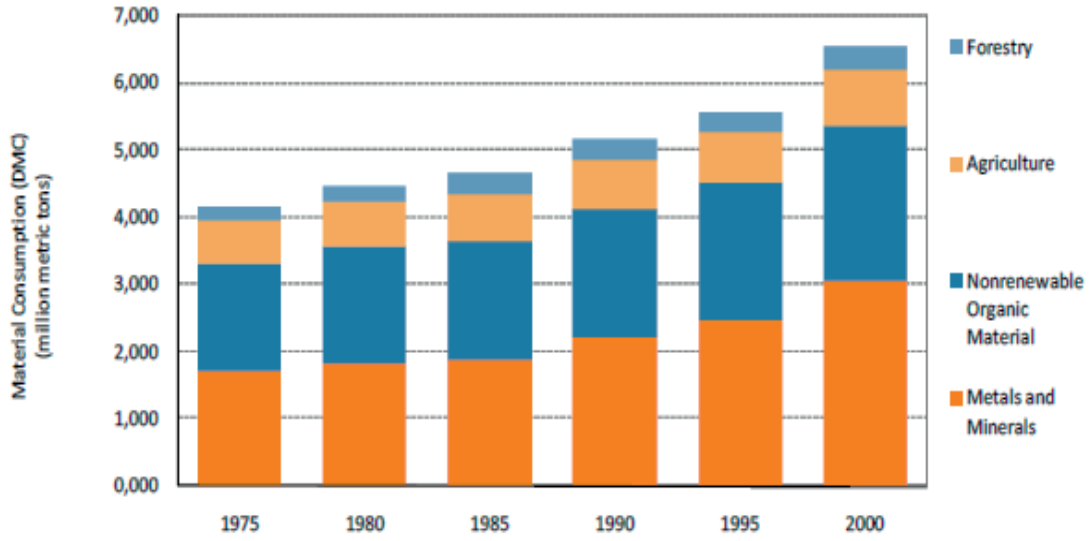


Fig. 6.4 Material consumption in the United States by Sector of Origin, 1975-2000 (Adapted from: WRI Material Flows Database 2005)

Persistent, bio accumulative, toxic chemicals (PBTs) cause adverse effects to humans and the environment because they have common characteristics:

1. PBTs have a high durability and degrade extremely gradually upon release into the environment.
2. The concentration of PBTs increase in animal and human bodies upwards in the food chain, as they are accumulated basically through food.
3. A large number of toxic effects in fish, wildlife, and humans, including effects on the nervous system, reproductive and developmental problems, immune-response suppression, cancer, and endocrine disruption have been caused by exposure to PBTs.
4. In addition, wind and water currents cause some PBTs to travel long ranges as air particulates or sediments.

6.3.1 Pollution Release Transfer Register (PRTR)

Pollutant release and transfer registers (PRTRs) are mechanisms for the collection and dissemination of data on environmental releases and transfers of toxic chemicals from industrial and other facilities. It brings together information about the type, quantity, place and amount of chemicals released.

PRTRs typically require facility owners or operators who release chemicals (e.g., in such industries as manufacturing and mining) to quantify their releases and to report them to governments on a regular basis. Reporting can be both on emissions from fixed sources (e.g., factory smokestacks) as well as from diffuse sources (e.g., mobile sources such as three wheelers, bikes, automobiles, trucks, aircraft and trains).

Depending on the threshold a government sets for reporting, facilities can range from large industrial sites to small operations such as dry cleaners. PRTRs currently exist and some examples are given below.

- Australia National pollutant inventory (NPI),
- Canada National Pollutant Release Inventory (NPRI),
- European Pollutant Release and Transfer Register (E-PRTR).
- Mexico Registro de Emisiones y Transferencia de Contaminantes (RETC),
- US Toxics Release Inventory (TRI).

The European Union is a party to the UNECE Protocol on PRTRs and created its own register, the European Pollutant Release and Transfer Register (E-PRTR). This register was established by Regulation (EC) No. 166/2006.

Therefore a PRTR is a mechanism to obtain regular, periodic information about releases and/or transfers of chemical substances of interest which is published as soon as possible and made public by Right to Know Acts. As such, a PRTR is a tool for promoting efficient and effective policies for environmental protection and sustainable development.

Elimination of PBTs through BAT and BEP

BAT-*Best Available Techniques*.

Under the Stockholm Convention, **BAT *(Best Available Techniques)*** are referred as '*the most effective and advanced stage in the development of activities and their methods of operation which reveals the practical suitability of particular techniques for providing in principle the basis for release limitations designed to prevent and, where that is not practicable, generally to reduce releases of chemicals listed in Part I of Annex C and their impact on the environment as a whole*' (Swain et al;1992).

BEP-*Best Environmental Practices*

Under the Stockholm Convention, **BEP *(Best Environmental Practices)*** are referred as *'the application of the most appropriate combination of environmental control measures and strategies*' (Swain et al;1992).

The European Union has initiated a directive in 2008 named as the Integrated Pollution Prevention and Control (IPPC). Under the above directive, a list of reference documents were drawn which encompassed BAT reference documents called as BREFs, ranging from ceramics, ferrous metals, milk, industrial cooling systems, iron and steel production. (European Commission 2018). Each document generally gives information on a specific industrial/agricultural sector in the EU, on the techniques and processes used in this sector, current emission and consumption levels, techniques to consider in the determination of the best available techniques (BAT) and emerging techniques. For each industry, a BREF describes the main findings, a summary of the principal BAT conclusions and the associated consumption and emission levels.

Practical examples of successful implementation of BAT and BEP in the City of Kitakyushu, Japan.

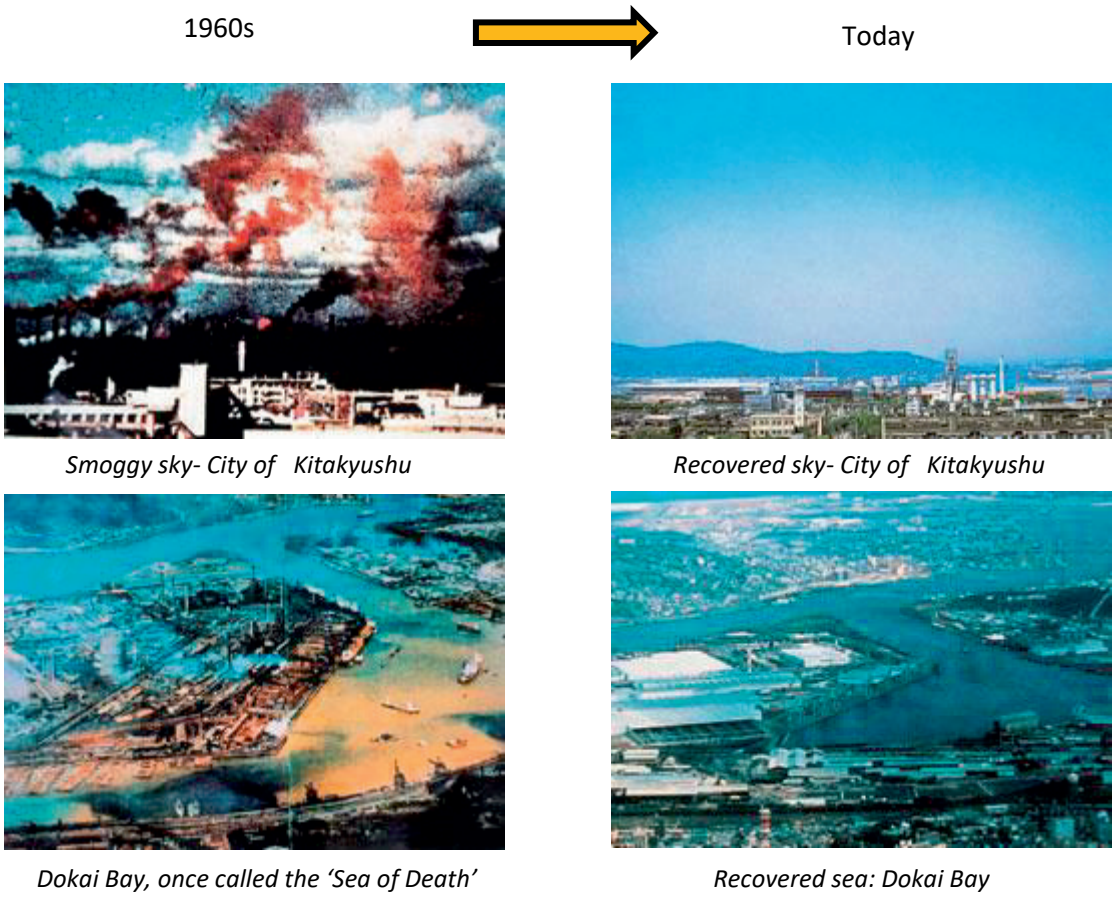


Fig. 6.5 Practical examples of successful implementation of BAT and BEP City of Kitakyushu, Japan (Adapted from: Stockholm Convention Overview of BAT and BEP)

6.3.2 Replacement Solution-*Alternatives*.

PBTs

- Remains **intact** for extremely **long time periods.**
- **Widely distributed** throughout the environment.
- **Undergoes accumulation** in the **lipid tissues** of **living beings.**
- **Toxic** to both **humans** and **other fauna.**

Use of Alternative substances

- Should not **exhibit** the **characteristics of PBTs.**
- Result in considerably **lower risk** than the **use of PBTs.**
- Should help **protecting** both **human health** and the **environment** from **PBTs.**

Source:http://chm.pops.int/Implementation/Alternatives/Overview/tabid/5834/Default.aspx

Many experts have stressed on the importance of alternative substances as a measure of reducing the impact of PBTs. Substitution of hazardous substances and mixtures with less hazardous alternatives is a basic principle of any good chemical risks management and legal requirement according to workplace legislation.

An online platform such as SUBSPORT offer free-of-charge, multilingual platforms for information exchange on alternative substances and technologies, as well as tools and guidance for substance evaluation and substitution management within the EU (Link at https://www.subsport.eu/about-the-portal). These online platforms sometimes contain interactive activities for users to request innovative non-hazardous materials to be used as alternatives for conventional hazardous substances. Examples include halogen-free flame retardant synergists, cleaning agents, water repellents and bleaching agents.

Generally the steps to replacing hazardous substances with alternatives are as follows. (Source: SUBSPORT)

1. **Define the Problem**

Identify the hazards and useful characteristics of the existing material. Describe the function of the substance and the conditions needed to make it work at the desired performance level: operational parameters (pH, temperature, etc.), quantity, and equipment.

2. Set substitution criteria

Set criteria to eliminate alternatives that are not safer or not safe enough. Use limits and regulations prescribed by regulations and legal bodies to set your criteria.

3. Search for alternatives

Make a list of possible alternatives after searching through public or private databases.

4. **Assess and compare alternatives**

Analyze the advantages and disadvantages of the list of possible alternatives considered in the above steps. Consider hazard criteria, operating costs and other benefits. Select the alternative which is safer, feasible and fits the nature and dimension of your problem.

5. Experiment on pilot

6. Implement and improve

Table 6.1 below lists the names, common uses, and exemptions/alternatives for "new POPs" that were listed in 2009 as well as endosulfan, which was added to the convention in 2011, and the flame retardant hexabromocyclododecane (HBCDD), which was added in 2014 (Swedish Chemicals Agency 2013).

Table 6.1: "New POPs" under the Stockholm Convention on persistent organic pollutants (Adapted from: Persistent, Bioaccumulative, and Toxic (PBT) Chemicals Technical Aspects, Policies, and Practices, 2016).

Name	Uses	Exemptions /Alternatives
Alpha hexachlorocyclohexane (alpha-HCH)	Pesticide and by-product; no current end-product uses	No exemptions
Beta hexachlorocyclohexane (beta-HCH)	Pesticide and by-product; no current end-product uses	No exemptions
Chlordecone	Pesticide; used as an agricultural insecticide, miticide, and fungicide	No exemptions
Hexabromobiphenyl	Industrial chemical, hexabromobiphenyl is an industrial chemical used as a flame retardant, mostly in the 1970s	No exemptions
Hexabromodiphenyl ether and heptabromodiphenyl ether (commercial octabromodiphenyl ether)	Industrial chemical; used as a flame retardant	Limited exemptions to account for articles containing the substance and to allow for recycling of materials containing the chemicals
Lindane	Pesticide and pharmaceutical agent; used as a broad-spectrum insecticide	Limited exemption for control of head lice and scabies
Pentachlorobenzene	Industrial chemical, pesticide, and by-product; was used in PCB products, in dyestuff carriers, as a fungicide, and as a flame retardant	No exemptions

Perfluorooctane sulfonic acid, its salts, and PFOS	Industrial chemical; used in production of polymers and in electronics, firefighting foam, photo imaging, hydraulic fluids, and textiles	Exemptions for use in manufacturing of certain products
Technical endosulfan and its related isomers	Pesticide; used as a broad-spectrum insecticide	Exemptions for use in controlling certain crop-pest complexes
Tetrabromodiphenyl ether and pentabromodiphenyl ether (-BDE) (commercial pentabromodiphenyl ether)	Industrial chemical; used as an additive flame retardant	Specific exemptions to account for articles containing the chemical and recycling of articles containing the chemical
Hexabromocyclododecane	Industrial chemical; used as an additive flame retardant in expanded, extruded, and high-impact polystyrene as well as textile coatings	Specific exemptions for use in expanded and extruded polystyrene for building applications

Most exemptions are effective for five years from the date of entry, and most of these exemptions entered into force on August 26, 2010 (technical endosulfan entered into force on October 27, 2012).

6.3.3 Reducing PBT Chemicals

- **Cross-media approach for all environmental legislation:** The current regulation systems focus on passing legislation that does not fully tackle the risks for cross-media transfer of PBTs after release. More attention should be paid to the collective processes on the land, air, water, and sediments.

- **Greater emphasis on prevention of pollution:** The contemporary, single-media approach results in a system that emphasizes the treatment, rather than the prevention of generation of pollution. PBTs are a special issue as their initial level of release may not be detectable until they've reached harmful levels. Efforts must be focused on prevention of the production of these PBTs.

"An ounce of prevention is worth a pound of cure"

– Benjamin Franklin



- **More effective measures to tackle each source of pollution:** The current approach is mostly based on large producers or dischargers of toxins, on the regulation of these PBTs in discharges, and approaching large cleanup sites. Though it is effective, many other sources still remain. All pollution sources must be addressed, even ones that come from individual and "non-point" sources.
- **Better information:** Businesses, and people currently lack the scientific, technical, economic and environmental information needed for the identification and implementation of sustainable measures to decrease and/or prevent chemical uses, releases and/or exposures. This information must be generated and made available, for the reduction and prevention of exposure to PBT chemicals and releases.
- **Precautionary approaches for tackling PBT chemicals:** Many regulation programs presently use policies that need agencies to quantify the problems caused by low levels of PBTs before taking action for prevention. In addition, reasonable preventive steps are often delayed when researchers can't precisely define all of the complex interactions between PBT releases and damage to environment. More precautionary approaches are needed for the prevention of the environmental damage related to PBTs.
- **Greater awareness of the issues and solutions:** Many individuals aren't aware of how daily activities contribute to the generation or release of PBTs. Common situations like driving a car or spilling oil on the road contribute to PBT release. Accessible public education should be provided so the public understands how daily activities contribute PBTs in the environment, and their role in prevention.
- **Integration of economic and environmental goals:** The current policies fail to systematically merge economic and environmental goals. This focus results in less integrated decision making, and lessens regulation of producing and releasing of PBTs. This is important

as many PBTs released are produced from daily activities that we highly rely on. A positive shift in our daily lifestyle should be made and even in the products that consumers buy.

6.3.4 Implementation of regulatory frameworks for PBTs

With the evidence of long-range transport of these substances to remote regions and the consequent threats they pose, many countries recognize that cooperative action for the sound management of these substances is needed. Therefore, several international and regional treaties have been implemented to address this issue. There are international and regional PBT policies whereas *international* and *regional* denotes the difference in geographical reach. The international apply globally, while the regional treaties have more limited applicability defined by geographic/jurisdictional boundaries.

6.3.4.1 International PBT conventions and treaties

There are several globally ratified conventions for the regulation and management of harmful chemicals and their adverse effects to human and environment;

- Basel Convention,
- Stockholm Convention,
- Rotterdam Convention,
- Montreal Protocol
- Minamata Convention

1. Basel Convention

The Basel Convention was adopted in 1989 for the improvement *monitoring and supervision of transboundary movement of hazardous wastes.*

The Basel Convention comprises of the below objectives:

- Reduction of movements of hazardous wastes across boundaries, in accordance with their environmentally sound management.
- Disposal of hazardous wastes in close proximity to their generation source.
- Minimizing the generation of hazardous wastes with respect to amount and toxicity.
- Prohibiting the export of hazardous waste to developing countries that lack suitable disposal mechanisms.

The Basel Convention enforces a very strict control system of operation on the basis of prior written notification procedures. The notification procedure of transboundary motion of

hazardous wastes or other wastes can only occur upon prior written notification to the relevant competent authorities of states of export, import and transit and upon permission from these authorities allowing the transboundary movement of waste. Any other movement of hazardous wastes or other wastes across boundaries done in opposition of notification system is considered as illegal traffic and subject to prosecution.

2. Stockholm Convention



The Stockholm Convention is an international treaty to protect human health and the environment from POPs. This Convention oversees the ban of 28 POPs. The text of the Stockholm Convention on Persistent Organic Pollutants was adopted in 22 May 2001 and entered into force on 17 May 2004;

The statutory parties to the Stockholm Convention are required to follow the following steps:

- Producing, using, importing, and exporting the 28 most dangerous POPs will be subjected to elimination or restriction. There is a special regulation with relevance to DDT at it is utilized in developing countries to combat malaria.
- Upon the construction of new plants/installations, steps must be undertaken to minimize the possible production of Persistent Organic Pollutants.
- An inventory should be present which lists stockpiles and wastes that are contaminated with POPs and they should be disposed in an environmentally sound manner.
- PCB containing devices are still permitted for use until 2025, but under several safety precautions and conditions.
- However by 2028, all PCB devices and equipment should be disposed of in an environmentally sound manner.

The PCBs Elimination Network (PEN) is a network that was launched at the simultaneous extraordinary meetings of the Conferences of the Parties to the Basel, Rotterdam and Stockholm Conventions in Bali on 22 February 2010. The PEN started as an agreement for exchange of information relevant to the promotion of the cost-effective completion of the environmentally sound management (ESM) of liquids and equipment containing or contaminated with PCBs.

In the Stockholm Convention, the following are banned:

- The production, trading and import of PCBs
- Reusing and processing PCB waste

- Refilling of equipment containing PCBs
- The eighth meeting was held in 2017 April- May in Switzerland and amended the list of POPs in consecutive years of 2009, 2011, 2013, 2015 and 2017. The list of POPs is categorized under three annexes; annex A (Elimination), annex B (Restriction) and annex C (Unintentional production).
- **Annex A (Elimination)** - Parties must take measures to eliminate the production and use of the chemicals listed under Annex A.
- **Annex B (Restriction)** - Parties must take measures to restrict the production and use of the chemicals listed under Annex B
- **Annex C (Unintentional production)** - Parties must take measures to reduce the unintentional releases of chemicals listed under Annex C with the goal of continuing minimization and, where feasible, ultimate elimination.

Rotterdam Convention (PIC Convention)



Pesticides and other dangerous PBTs are responsible for the deaths and diseases of several thousand people every year. In addition they poison the natural ecosystem and destroy many wild species of fauna. Countries started to look towards this issue in the 1980s decade by starting a voluntary Prior Informed Consent (PIC) procedure. The PIC required exporters who are engaged in trade of a list of hazardous substances, to obtain the prior informed consent of the corresponding importers before engaging with the transaction.

A first line of defense was established by the Convention by providing the countries of import with the data and information they need to recognize potential dangers and remove chemicals they can't safely handle. Upon agreement of a country to import chemicals, the Convention promotes their safe utilization through labelling standards, technical assistance, and further support. In addition, it makes sure that exporters obey the criteria. The Rotterdam Convention was enforced on 24 February 2004. The contracting parties take steps to:

- Establishment of an official notification procedure e.g. informing the nation of import that an export of a chemical present in the PIC list will occur before the first shipment.
- Informing the importing nation that an export of a chemical that is prohibited or severely confined for use within its territory will occur before the first shipment
- Informing other nations of every other state ban or severe restriction of a chemical.

3. Montreal Protocol

The Montreal Protocol on Substances that Deplete the Ozone Layer was an international agreement that was agreed on 26 August 1987, and entered into force on 26 August 1989 with the intent of protecting the ozone layer by phasing out Ozone Depleting Substances (ODS). The treaty has been ratified by all United Nations members, as well as Niue, the Cook Islands, the Holy See and the European Union. The treaty is centered on the cessation of the use of several halogenated hydrocarbons including CFCs (Chlorofluorocarbons). Action was enforced on phasing out almost 98% of ODS by the end of the year 2014. As a consequence, the hole in the Ozone Layer above the Antarctic is gradually recovering. The Montreal Protocol has been cited as one of the most successful environmental agreements to date.

4. Minamata Convention

The Minamata Convention on Mercury is an international treaty designed to protect human health and the environment from human related emissions and releases of mercury and mercury related compounds. The treaty was signed in 2013 in Japan and currently has 128 signatories. The agreement addresses the direct mining of mercury, its trade, safe storage and disposal in the form of waste. The Minamata Convention controls a wide range of products containing mercury, the manufacture, import and export of which will be altogether prohibited by 2020, except where countries have requested an exemption for an initial 5-year period. These products include certain types of batteries, of lamps such as compact fluorescent lamps, of and relays, soaps and cosmetics, thermometers, and blood pressure devices. Dental fillings which use mercury amalgam are also regulated under the Convention, and their use must be phased down through a number of measures. The importance of the Minamata Convention for Sri Lanka is immense as the country is situated in proximity to the two highest mercury producing countries on Earth: China and India respectively.

6.3.4.2 Regional PBT policies

It is to be noted that the major exclusive regional treaties of the South Asian and Indian Ocean region such as BIMSTEC (Bay of Bengal Initiative for Multi-Sectoral Technical and Economic Cooperation) and IORA (Indian Ocean Rim Association) do not have any significant attention towards PBTs. Following are some of the major regional agreements for the control and management of PBTs.

- Oslo–Paris Convention,
- REACH Regulations - EU.
- Barcelona Convention.

1. Oslo–Paris Convention for the Protection of the Marine Environment of the North-East Atlantic

The Oslo–Paris (OSPAR) Convention, which was enforced in 1998, is an agreement among fifteen nations in Northwestern Europe and the European Union to conserve the marine ecosystem of the North-East Atlantic. To achieve that objective, annexes are included which concentrates on the prevention and removal of pollution from land-based sources, dumping or incineration, and offshore sources, in addition to an annex on environmental quality assessment.

In order to complete the obligations of the convention and subsequent annexes, the OSPAR Commission created the North-East Atlantic Environment Strategy, which includes five thematic schemes: 1.biodiversity, 2.eutrophication, 3.radioactive substances, 4.offshore oil and gas industry, and 5. hazardous substances that present risks to environments in the North-East Atlantic. The PBT concept is assimilated into the annexes and the Hazardous Substances Strategy. The definition of "hazardous substances" by OSPAR is those *that are persistent, bioaccumulative, and toxic, as well as substances of "equivalent concern"* (OSPAR Commission 2010a).

Annex I (pollution from land-based sources) and Annex III (pollution from off-shore sources) identify Persistent Bioaccumulative Toxic chemicals (and substances of equivalent concern) as targets for release reduction and phasing-out. The goal of the Hazardous Substances Strategy is to decrease discharges of hazardous chemicals "*with the aim to achieve concentrations in the marine environment near background values for naturally occurring substances and close to zero for manmade synthetic substances*" (OSPAR Commission 2010a, Part II, Hazardous Substances paragraph 1.1).

2. EU: Registration, evaluation, authorization, and restriction of chemicals (REACH).

Several European Union legal channels tackle PBTs with an example such as REACH under technical administration by the ECHA (European Chemicals Agency) and decisions of policy done by the European Commission. REACH is a composite assembly of several regulatory bodies that manage the cradle-to-grave manufacture, importation, trade, and utilization of industrial chemicals. Per law of the EU, REACH comprises of a regional policy; although, it shares many common characteristics with nationwide programmes.

As per the name, the REACH Regulation is comprised of four discrete, but linked, programmes: 1.registration, 2.evaluation, 3.authorization, and 4.restriction. Under *registration*,

nearly all new and current chemical substances manufactured and sold in Europe above the amount of 1 ton per year must undergo registration with ECHA. Under a complementary chemical *evaluation* process, Member States coordinated by ECHA analyze the hazards linked to a lesser number of chemicals of concern. REACH focuses on "substances of very high concern" (SVHCs) such as CMRs (Carcinogenic, mutagenic, reprotoxic substances) and PBTs for potential hazard management. Under REACH, SVHCs are put on a Candidate List to signify that they are candidates for *authorization*. Chemicals on the Authorization List undergo a mandatory phase-out and substitution, unless the industry fulfils strict conditions with evidence through a use-specific authorization process. In addition, The European Union can introduce *restrictions* on specific uses of substances to tackle "unacceptable risks" such as PBTs or CMRs.

5. UNEP/MAP-Barcelona Convention and its Protocols

The UNEP/MAP-Barcelona (United Nations Environment Programme/Mediterranean Action Plan) Convention for the Protection of the Marine Environment and the Coastal Region of the Mediterranean was initiated in 1995 thus amending the Barcelona Convention on the protection of the Mediterranean Sea against pollution adopted earlier in 1976 by the Mediterranean coastal nations and European Union. The Barcelona Convention is supplemented by 7 significant protocols out of which 2 tackle separate viewpoints of POPs management namely 1. The Land based sources and activities Protocol, 1996 (LBS Protocol) and 2. The Protocol on the transboundary movement of hazardous waste in the Mediterranean, 1996.

DICTIONARY

Carcinogenic: Capable of causing cancer

Mutagenic: Capable of causing genetic mutations

Reprotoxic: Capable of interfering with the reproductive system.

The LBS Protocol allows the contracting parties to initiate legislative measures to remove a number of chemicals including PCBs and their stocks, in agreement with the commitments and framework of the Stockholm Convention.

6. Malé Declaration on Control and Prevention of Air Pollution and Its Likely Transboundary Effects for South Asia

In 1998, the United Nations Environment Programme (UNEP), together with the Stockholm Environment Institute (SEI) drew attention to the possibility of the impacts of transboundary air pollution in South Asia. This initiative led to the adoption of the Malé Declaration on Control and Prevention of Air Pollution and its Likely Transboundary Effects for South Asia. The Malé Declaration's objective is to aid the process of providing a clean environment through clean air. The Declaration calls for regional cooperation to address the increasing threat of transboundary air pollution and its possible impacts. The eight member countries of Malé Declaration include Bangladesh, Bhutan, India, Iran, Maldives, Nepal, Pakistan and Sri Lanka.

6.3.5 Other Measures of National Scale

PBTs are an increasing problem to Sri Lanka because of increasing proof and evidence which show that PBTs cause chronic adverse impacts to our health and the surrounding environment. Various processes are responsible for the production and release PBTs into the environment which may be highly visible sources such as large industrial processes which have been the conventional approach of pollution control schemes. Nevertheless, there are a number of lesser sources of PBTs that altogether can emit an equal or greater PBT amount. Examples of these lesser (usually "non-point") sources include motor vehicles, consumer products, and agricultural and home-use pesticides.

Though a number of chemicals have adverse effects on humans and the ecosystem, PBTs are a challenge to regulation mainly due to their characteristic properties. In cases where non-PBT chemicals are emitted into the environment under permit, the concentration of the chemicals gradually decrease or dilute as they travel from the original source and are subject to dispersion. In addition they may degrade due to reactions with other chemicals or due to photolysis. By the time of exposure to the chemicals, the concentration is extremely diluted so that it is does not pose any health risk.

PBTs don't degrade or undergo reaction with other chemicals as easily as they have a persistent existence. They bind to fat containing adipose tissues in living beings. These two features prevent PBTs from dilution as they travel away from a source. Most of the time, their concentration can actually multiples significantly in the environment. As PBTs travel "up the

food chain", their concentrations can expand as they accumulate in the fat of fauna such as fish, poultry, and cows. This concept is illustrated in Fig. 6.6.

Releases from current and historical sources have caused elevated levels of PBTs in the air, water, soils, and sediments throughout Sri Lanka. For example, many PBT chemicals have congregated in water bodies, sediments and fish tissue to levels which need preventive actions from the Sri Lankan Central Environmental Authority (CEA-SL) and Municipal Councils of

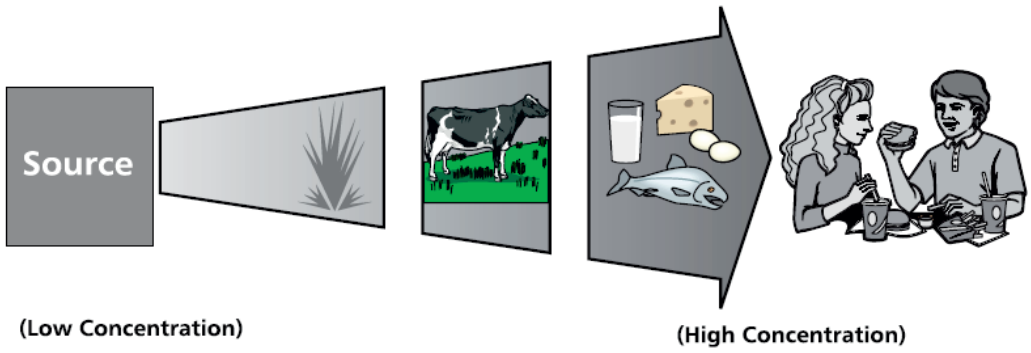


Fig. 6.6 As PBTs move up the food chain, their concentrations can increase (Adapted from: Draft Strategy to Continually Reduce Persistent, Bioaccumulative, Toxic Chemicals

individual districts to clean up these waters and prevent further degradation.

6.3.5.1 Regulatory Structure in Sri Lanka

Pesticides are regulated in Sri Lanka through the enforcement of the **Control of Pesticides Act No 33 of 1980**. The Department of Agriculture of the Ministry of Agriculture has the mandate to implement the Act. There are regulations on industrial PBT chemicals except PCBs, prohibiting them for use in electrical transformers.

6.3.5.2 International Agreements

As described previously in this chapter, Sri Lanka has ratified/signed the international agreements relating to chemicals and the environment such as the Basel Convention on Transboundary movement of Hazardous Wastes, the Montreal Protocol on Ozone layer depleting substances and the Stockholm convention on POPs. The Rotterdam convention on PIC was yet to be signed but it was enforced voluntarily from the early nineties. It was later ratified in 2006. A national implementation plan is already underway in Sri Lanka for the Stockholm Convention with the assistance of GEF/UNEP (Global Environment Facility/ United Nations Environment Programme).

6.3.5.3 Current PBT Management Strategy

The regulatory authorities are closely linked up with the relevant international agencies, which had enabled them to take action on PBT pesticides. London Guidelines (amended 1989) and the PIC voluntary scheme have paved the way to prohibit the use of most chlorinated hydrocarbon pesticides more than a decade ago. For those prohibited pesticides, safer alternatives have been either recommended or found redundant in chemical pest control.

Though it was not considered as a chlorinated hydrocarbon for regulatory actions, endosulfan was banned in 1998 along with some other PTS (Persistent Toxic Substances), because the formulation marketed was in the WHO hazard class I-b, despite its technical grade being in class II. Sri Lanka has a national policy, implemented in 1995 that no pesticide formulations of WHO hazard classes I-a and I-b are marketed for regular pest control purposes in agriculture (WHO, 2008).

There is no monitoring scheme (or regulation) for the control of unintended by-products. The Central Environmental Authority (CEA) of the Ministry of Environment regulates industrial emissions through the provisions of the Environment Act. Environmental Protection Licenses are issued by the CEA after careful assessment of the industry, its activities and the environmental protection measures adopted to make sure that they meet National Emission Standards. Disposal of Municipal Solid Wastes are regulated according to the directives issued by the CEA to the local authority, under the legal provisions vested on them to take necessary action to manage municipal solid wastes.

Although all PCB-containing transformers have been replaced, there are no proper monitoring schemes for the prevention of the import of any such PCB-contaminated items into the country. The currently recovered PCBs are in safe storage. Organotin compounds are used in the ship industries, which are carried out in the Colombo harbor area, where the items do not have to be legally imported into the country through regular Customs procedures.

In the midst of these management strategies, the use of cement kilns to burn PCBs instead of storing them has shown great promise and could be a best practice in the disposal of PCBs in the future as well (Karstensen et al., 2010), even in Sri Lanka as most developing countries do not have specialized hazard waste incinerators.

The way ahead for control and management of PBTs in Sri Lanka

High fish consumption in Sri Lanka ⇒ Seek local fish advisories/guidance

Improve fish cleaning/cooking methods ⇒ Remove Fat layer

Proper awareness programs ⇒ Advocate elimination of POPs from industrial sources, waste incineration and power generation

Proper cleaning procedures ⇒ Request cleaning of contaminated sites and sediments

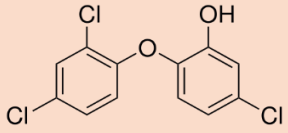
Promote awareness through research ⇒ International, collaborative research on PBT control and management in environmental compartments.

International agreements ⇒ Support to eliminate PBTs from the world.

Further facts

Triclosan is an antibacterial and antifungal agent found in some consumer products, including toothpaste, soaps, detergents, toys, and surgical cleaning treatments. Triclocarban is an antibacterial agent common in personal care products like soaps and lotions. Usually they are contaminated with dioxins. Have a look at the video below of the Florence Statement on the hazards on triclosan and triclocarban in consumer products.

https://www.youtube.com/watch?v=slXHCzbSTPY



Structure of Triclosan

Table 6.2: Tolerance limits for the discharge of industrial waste, waste from rubber factories, textiles and tanning industry (Adapted from: NATIONAL ENVIRONMENTAL ACT, No. 47 OF 1980)

No.	**Industry type** ➡	Industrial Waste			Waste from rubber factories	Textile industry	Tanning industry	
	Discharge Environment ➡ / ⬇	Inland surface water	Land for irrigation purpose	Marine coastal areas	Inland surface water **(Type I factory/ Type II factory)**	Inland surface water	Inland surface water	Marine coastal areas
	Parameter (mg/L – Max)							
1	BOD	30	250	100	60/ 50	60	60	100
2	Phenolic Compounds (as C_6H_5OH)	1		5		1.0	1.0	5.0
3	COD	250	400	250	400/ 400	250	250	300
4	Total residual chlorine	1.0		1.0				
5	Ammonical Nitrogen (as N)			50	300/ 40	60		
6	Total Nitrogen (as N)				300/ 60			
7	Chlorides (as Cl)		600			70	1000	
8	Sulphates (as SO_4^{2-})		1000					
9	Boron (as B)		2.0					
10	Flourides (as F)	2.0		15				
11	Sulphide (as S)	2.0		5.0				
12	Arsenic (as As)	0.2	0.2	0.2				
13	Cadmium (as Cd)	0.1	2.0	2.0				
14	Chromium, total (as Cr)	0.5	1.0	2.0		2.0	2.0	2.0

15	Chromium, hexavalent (as Cr^{6+})	0.1		1.0		0.5	0.5	0.5
16	Copper (as Cu)	3.0	1.0	3.0		3.0		
17	Iron (as Fe)	3.0						
18	Lead (as Pb)	0.1	1.0	1.0				
19	Mercury (as Hg)	0.0005	0.01	0.01				
20	Nickel (as Ni)	3.0		5.0				
21	Selenium (as Se)	0.05		0.1				
22	Zinc (as Zn)	2.0		5.0		5.0		
23	Pesticides	0.005		0.005				
24	Organo-Phosphorus compounds			1.0				
25	Chlorinated hydrocarbons (as Cl)			0.02				

Type I Factory - Latex Concentrate, Type II Factory - Standard Lanka Rubber, Crepe Rubber and Ribbed Smoked Sheet

7 Functional Characteristics of PBTs

7.1 General Aspects

Persistent, Bio-accumulative, Toxic chemicals (PBTs) are chemicals that have a global risk due to the ability for long-distance transport, persistence which delays degradation, undergoing biomagnification and bioaccumulation in environments, as well as their significant negative effects on human health and the environment (van Wijk *et al*; 2009). Humans are exposed through consumption of food, in addition through breathing contaminated air.

In our daily lives, we use many POPs containing products, which are additives to improve product performance, such as flame retardants or surfactants due to their chemistry (Lohmann *et al;* 2007). Most of the POPs are organo-halogens (Jones and Voogt; 1999). Therefore, POPs are ubiquitous on Earth in measurable levels. The widely used type of POPs are organochlorine pesticides, such as DDT and industrial chemicals, such as polychlorinated biphenyls (PCB). In addition they may include unintentional by-products of many industrial and incineration processes, especially polychlorinated dibenzo-p-dioxins (PCDD) commonly known as 'dioxins' and dibenzofurans (PCDF).

POPs bio-magnify throughout the food chain and bio-accumulate in organisms (Gobas *et al*; 2009). Therefore the highest concentrations of POPs are found in top level predators at the highest trophic levels of the food chain. As humans too occupy this position, background levels of POPs are also observed in the human body. The non-polar nature of these chemicals has resulted in a lipophilic nature, thus they show a tendency to dissolve in the fat layers of these organisms. When considering human exposure, even to small concentrations of POPs in some instances can lead to increased cancer risk, reproductive disorders, alteration of the immune system, neurobehavioral impairments, endocrine disruption, Geno toxicity and increased birth defects (Vasseur and Cossu-Leguille; 2006).

DICTIONARY

Genotoxicity is defined as the ability of chemicals to damage the genetic information within a cell.

Initially 12 Persistent Organic Pollutants were identified as being capable of causing negative impacts on humans and the environment which are divided in 3 subsets:

1. **Pesticides**: aldrin, chlordane, DDT, dieldrin, Endrin, heptachlor, hexachlorobenzene, mirex, toxaphene;
2. **Industrial chemicals:** hexachlorobenzene, polychlorinated biphenyls (PCBs)
3. **By-products:** hexachlorobenzene; polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/PCDF), and PCBs.

Afterwards after numerous revisions, the following chemicals were also added to the above list, which were collectively termed as new POPs.

1. **Pesticides**: Alpha hexachlorocyclohexane, Beta hexachlorocyclohexane, Chlordecone, Lindane, Pentachlorobenzene, Pentachlorophenol and its salts and esters, Technical endosulfan and its related isomers
2. **Industrial chemicals:** Decabromodiphenyl ether (commercial mixture, c-decaBDE), Hexabromobiphenyl, Hexabromocyclododecane, Hexabromodiphenyl ether and heptabromodiphenyl ether (commercial octabromodiphenyl ether), Hexachlorobutadiene, Pentachlorobenzene, Perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride, Polychlorinated naphthalenes, Short-chain chlorinated paraffins (SCCPs), Tetrabromodiphenyl ether and pentabromodiphenyl ether (commercial pentabromodiphenyl ether)
3. **By-products:** Pentachlorobenzene, Polychlorinated naphthalenes

Similarly, the chemical properties of heavy metals also play an important role in various aspects like usage and toxicology, compared to the physical properties like density. Out of these heavy metals lead, cadmium, mercury, arsenic and chromium are considered to cause more detrimental effects on living organisms.

7.2 Functional Characteristics of Aldrin

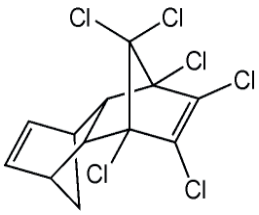


Fig. 7.1 Structure of Aldrin

Aldrin is a white crystalline solid. The common trade names of Aldrin are Aldree, Aldrex, Drinex, Octalene, Seedrin. Aldrin is sparingly soluble in water and non-flammable. These are extremely soluble in organic solvents. Aldrin is stable in the presence of organic and inorganic bases, hydrated metal chlorides and mild acids. Moreover, it is thermally stable up to 400 ^{o}C and pH levels from 4 to 8. Even though, Aldrin is stable over 200 ^{o} C and pH levels from 4 to 8, the unchlorinated ring is attacked by oxidizing agents and concentrated acids. The unchlorinated methano-bridge of aldrin could be replaced by 9-*syn*-Cl-CH- and that of isodrin by -CH_2CH_2- or spirocyclopropane, but the overall molecular length cannot exceed that delineated by dieldrin or alpha-endosulfan. There were, however, interesting indications that some of the chlorine atoms in

the hexachloronorbornene moiety could be replaced by hydrogen (Brooks; 2010). When heated to decomposition, it emits toxic fumes of hydrogen chloride. It is non-corrosive to steel, brass, Cu, Ni and Al, yet it causes corrosion of these metals due to the slow evolution of HCl during storage. Residual aldrin occurs readily in soil due to microbial interaction. The nonpolar nature of Aldrin and its low solubility in water enhance binding to soil particles, leaving little potential for leaching to groundwater. Aldrin can kill birds, fish, and humans.

Do you know? : The fatal dose for an adult male human is calculated to be about 5g.

7.3 Functional Characteristics of Chlordane

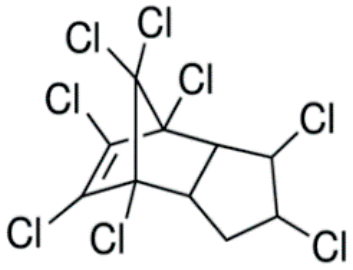


Fig. 7.2 Chemical structure of Chlordane

Chlordane is retained in soil for long periods and has an observed half-life of 1 year. With regard to the solubility characteristics, it is soluble with aliphatic and aromatic hydrocarbon solvents, including deodorized kerosene while being insoluble in water. It loses its chlorine presence in the presence of alkaline reagents and should not be formulated with any solvent, carrier, diluent or emulsifier which has an alkaline reaction (PubChem; 2010).Technical Chlordane is a viscous liquid made of a mixture of compounds that are solids when pure. Chlordane may be lethal to birds and fish but the lethality is dependent on the type of species, with mallard ducks, bobwhite quail, and pink shrimp being fatal victims. Chlordane can have an impact on the human immune system and a possible human carcinogen.

7.4 Functional Characteristics of DDT

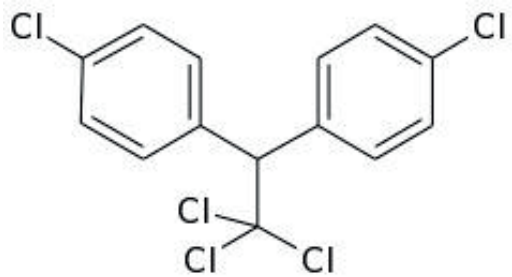


Fig. 7.3 Chemical structure of DDT

Do you know? : DDT, prepared by the reaction of chloral with chlorobenzene in the presence of sulfuric acid, **was first made in 1874** and its insecticide property was recognized later, which earned the discoverer of the insecticide property, Paul Müller a Nobel Prize in Medicine in 1948.

DDT has a very persistent stability of 10-15 years in soil and its widespread and abundant utilization have resulted in DDT residues being

ubiquitous, even appearing in the Arctic. DDT has a very low solubility in water and has a high solubility in most organic solvents. It can undergo partitioning into the atmosphere as a result of its semi volatility. DDT can be broken down in the environment. The breakdown products of DDT are illustrated in the Figure 7.4 below.

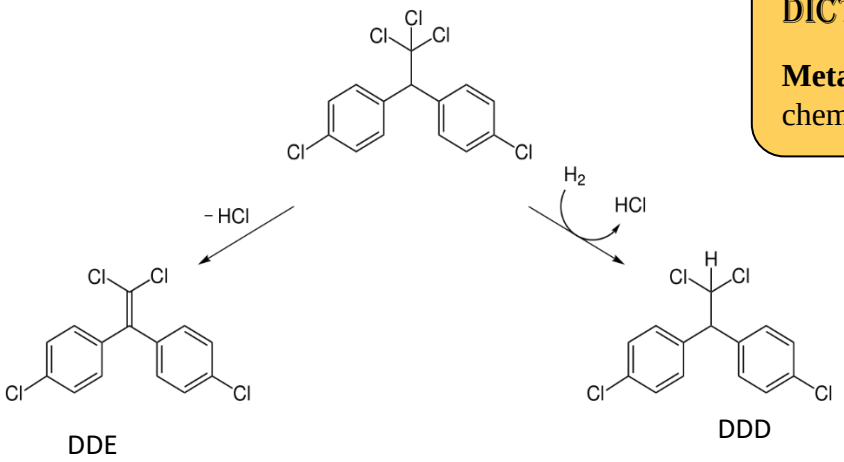


Fig. 7.4 The breakdown products of DDT

DICTIONARY

Metabolite: Reactant or product of a chemical reaction in a living

DDE-*1,1-dichloro-2,2-bis-4-chlorophenylethylene*

DDD- *1,1-dicholoro-2,2-bis-4-chlorophenylethane*

DDE-*1,1-dichloro-2,2-bis-4-chlorophenylethylene* and **DDD-** *1,1-dicholoro-2,2-bis-4-chlorophenylethane* are also ubiquitous and have greater persistence than the parent compound. Here, DDE is a metabolite of DDT and DDE is produced when DDT in the soil is digested by soil bacteria. DDE is more persistent in the environment compared to DDT while DDE is less toxic than DDT. DDT is normally a whitish amorphous powder (Tang *et al*; 1999).

7.5 Functional Characteristics of Dieldrin

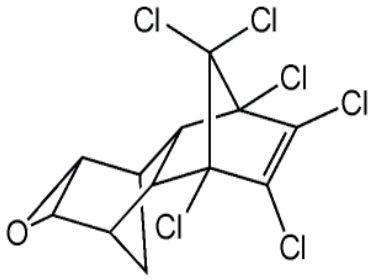
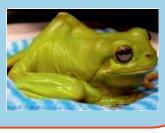


Fig. 7.5 Chemical structure of Dieldrin

Dieldrin has a half-life of roughly five years in soil. Dieldrin can be rapidly formed due to the conversion from Aldrin, therefore the dieldrin concentration in the environment is higher than its actual use.

The chemical formula of Dieldrin is $C_{12}H_8C_{16}O$ and the generic trade names are Alvit, Octalox, Quintox etc. These are found as a whitish or brownish powder. This is moderately soluble in organic solvents and non-flammable. (Shen and Wannia; 2005)

Do you know? : Dieldrin has a high toxicity to fish and other aquatic fauna, particularly frogs. Spinal deformities are known to develop in frog embryos after low level exposure.



Residues of dieldrin have been detected in air, water, soil and in organisms such as fish, birds, and mammals, including humans.

7.6 Functional Characteristics of Endrin

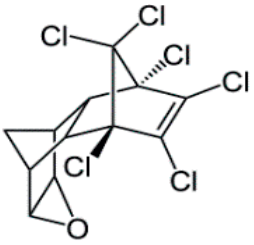


Fig. 7.6 Chemical structure of Endrin

Animals have the ability to break down Endrin, therefore as a result, it does not undergo accumulation in fatty tissue to the amount that other structurally similar chemicals do. Endrin possesses a long half-life, up to 12 years in soil. Endrin is a white crystalline solid with a melting point of 235°C. It is moderately soluble in water at 25°C. There is only limited information about the properties of Endrin aldehyde (an impurity and breakdown product of Endrin) or Endrin ketone (a product of Endrin, upon exposure to light).

7.7 Functional Characteristics of Heptachlor

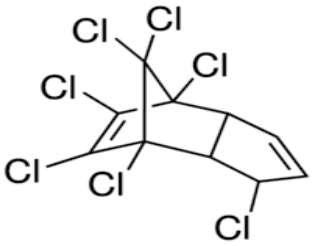


Fig. 7.7 Chemical structure of Heptachlor

Heptachlor is a white crystalline solid with a camphor-like odor. This is soluble in most organic solvents. Heptachlor and metabolites are white to light tan waxy looking solids. They are noncombustible, insoluble in water and toxic by inhalation, skin absorption or ingestion. Heptachlor is corrosive to metals.

7.8 Functional Characteristics of Hexachlorobenzene (HCB)

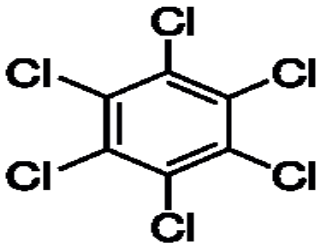
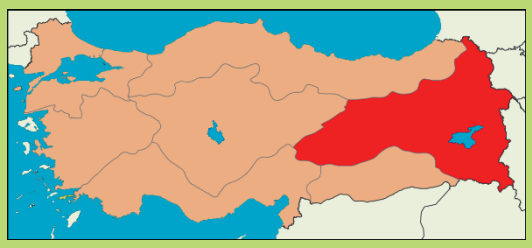


Fig. 7.8 Chemical structure of HCB

HCB is highly persistent in the environment as a result of its high stability and resistance to biological breakdown. HCB is a white crystalline solid that has an extremely low solubility in water. In high doses, HCB is lethal to some animals and, at lower levels, adversely affects their reproductive success. HCB has been found in food of all types.

Case File 5

After consumption of HCB-treated seed grain in eastern Turkey during the time period of 1954 and 1959, several symptoms arose, including photosensitive skin lesions, colic, and debilitation. About a 1000 people underwent a metabolic disorder called *porphyria turcica*, and which lead to the death of 14%. HCB was passed to infants by mothers through breast milk and the placenta.





Porphyria cutanea tarda symptoms

7.9 Functional Characteristics of Mirex

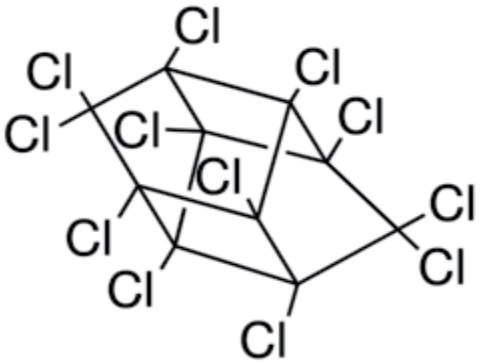


Fig. 7.9 Chemical structure of Mirex

Mirex is a snow white crystalline solid which undergoes thermal decomposition at 485^{o}C.

Though injury to humans has not been reported due to direct exposure to Mirex, research conducted on laboratory animals have resulted in its classification as a probable human carcinogen. Mirex has been proven toxic to several species of plant, fish and crustaceans.

7.10 Functional Characteristics of Toxaphene

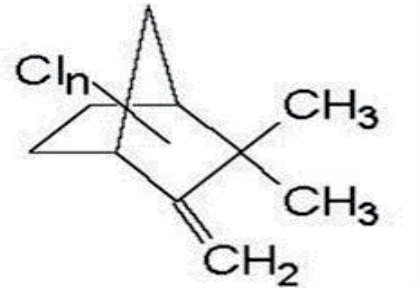


Fig. 7.10 Chemical structure of Toxaphene

Toxaphene has a half-life in soil for up to 12 years. Toxaphene is a yellowish waxy solid with a mild turpentine-like odor. This has a sparing solubility in water and has a high solubility in aromatic hydrocarbons.

Do you know? : Toxaphene has an elevated toxicity to fish; brook trout subjected to exposure for ninety days underwent a 46% reduction in weight and decreased the egg viability, while long-term exposure to levels of 0.5 g $L^{-1}$of water reduced egg viability to 0.



7.11 Functional Characteristics of Polychlorinated biphenyls (PCB)

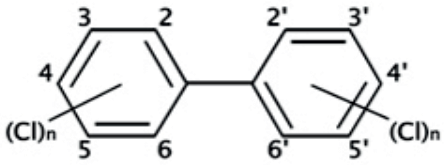


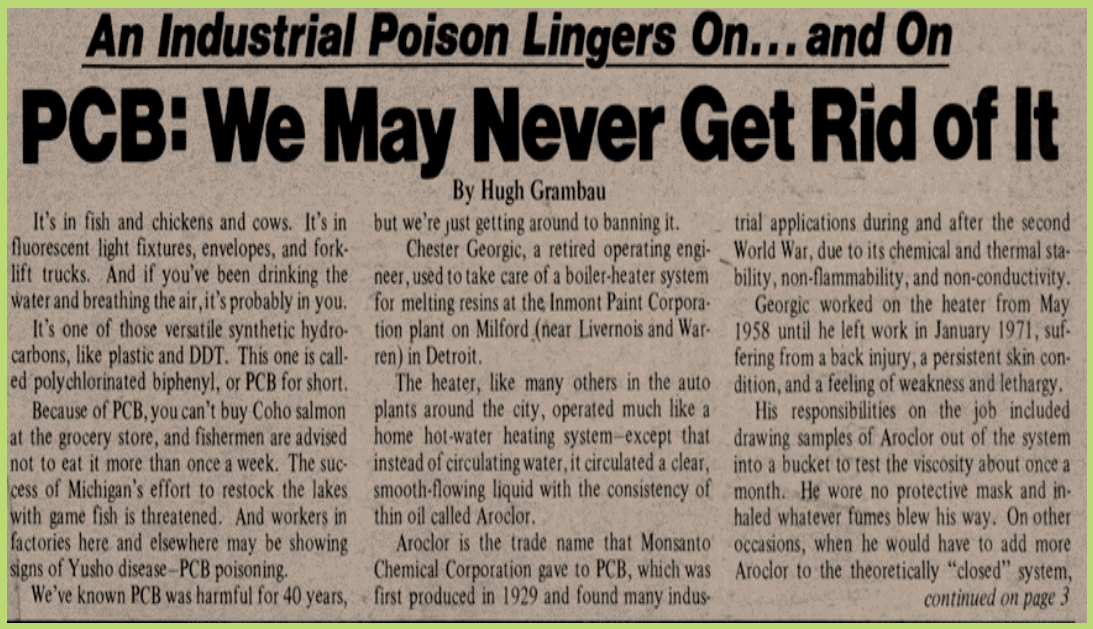
Fig. 7.11 Chemical structure of PCB

The persistence of PCBs is directly proportional to the degree of chlorination, and their half-lives may range from 10 days to one-and-a-half years. The number of chlorine atoms attached to the biphenyl groups of PCBs range from 2 to 10. A number of homologous PCB molecules exist that have different isomeric structures. PCBs are generally inert so they do not undergo reactions with both acids and alkalis and are thermally stable.

Case File 6

Massive exposures of PCBs have occurred through consumption of contaminated food. PCB-contaminated rice oil in Japan in 1968 and in Taiwan in 1979 resulted in pigmentation of nails and mucous membranes, and swelling of the eyelids, along with fatigue, nausea, and vomiting. Even seven years after the Taiwan incident, children born to mothers showed developmental delays and behavioral problems due to the persistent existence of PCBs in the mothers' bodies.

Likewise children of mothers who consumed elevated amounts of contaminated fish from Lake Michigan were observed to exhibit poorer short-term memory function. PCBs engage in immune system suppression are possible human carcinogens.



An Industrial Poison Lingers On...and On

PCB: We May Never Get Rid of It

By Hugh Grambau

It's in fish and chickens and cows. It's in fluorescent light fixtures, envelopes, and fork-lift trucks. And if you've been drinking the water and breathing the air, it's probably in you.

It's one of those versatile synthetic hydrocarbons, like plastic and DDT. This one is called polychlorinated biphenyl, or PCB for short.

Because of PCB, you can't buy Coho salmon at the grocery store, and fishermen are advised not to eat it more than once a week. The success of Michigan's effort to restock the lakes with game fish is threatened. And workers in factories here and elsewhere may be showing signs of Yusho disease–PCB poisoning.

We've known PCB was harmful for 40 years, but we're just getting around to banning it.

Chester Georgic, a retired operating engineer, used to take care of a boiler-heater system for melting resins at the Inmont Paint Corporation plant on Milford (near Livernois and Warren) in Detroit.

The heater, like many others in the auto plants around the city, operated much like a home hot-water heating system–except that instead of circulating water, it circulated a clear, smooth-flowing liquid with the consistency of thin oil called Aroclor.

Aroclor is the trade name that Monsanto Chemical Corporation gave to PCB, which was first produced in 1929 and found many industrial applications during and after the second World War, due to its chemical and thermal stability, non-flammability, and non-conductivity.

Georgic worked on the heater from May 1958 until he left work in January 1971, suffering from a back injury, a persistent skin condition, and a feeling of weakness and lethargy.

His responsibilities on the job included drawing samples of Aroclor out of the system into a bucket to test the viscosity about once a month. He wore no protective mask and inhaled whatever fumes blew his way. On other occasions, when he would have to add more Aroclor to the theoretically "closed" system,

continued on page 3

Headline from Ann Arbor District Library

All types of PCBs have a lipophilic nature and their lipophilicity is directly proportional to the degree of chlorination. They have an extremely solubility in water. PCBs with a lower degree of chlorination have more volatility than PCBs which are highly chlorinated. Pure individual PCB congeners are colorless and often crystalline. Even at low temperatures commercial PCB mixtures don't crystallize and exist as clear to light yellow oils or resins. Usually the solubility of PCBs is inversely proportional to increasing chlorination. Nevertheless, PCBs have a high solubility in

nonpolar organic solvents and biological lipids such as fat and oil. This property of PCBs leads to the bioaccumulation in the adipose (fat) tissue of the animals in the higher trophic levels of food chains. These are used as fire resistant materials because of their high flash points (170 – 380 °C). They result in vapours which are heavier than air, which are not explosive. This characteristic has caused them to be utilized in welding oils. In addition they possess a low electrical conductivity, high thermal conductivity and high resistance to thermal degradation. On the basis of these properties, they have been used as dielectric isolators in electrical equipment (WHO; 2008). The global dissemination of PCBs, implies that PCBs are subject to transport in air. The ability of PCBs to undergo deposition, volatilization from landfills into the atmosphere (adsorption to aerosols with a particle size of < 0.05–20 µm), and resistance to breakdown at low incineration temperatures which results in atmospheric transport as the main type of global circulation. In a USA study, 92% of detected PCBs were in the vapor phase. In a German study, PCBs types with low chlorination degrees were abundant in filtered air, while PCBs with a high chlorination were abundant in aerosols and rainfall. PCBs have a high toxicity to fish, with higher doses being fatal and resulting in failure to spawn at lower doses. Studies have shown that reproductive failure and immune system suppression in different wild fauna are linked to PCBs. e.g.: seals and minks.

DICTIONARY

Flashpoint: the temperature at which a certain organic compound releases sufficient vapour to ignite in air

7.12 Functional Characteristics of Polychlorinated dibenzo-p-dioxins (PCDD)

Seventy five different dioxins are present, out of which 7 are taken to be of risk. One dioxin congener persisted in the soil 10 - 12 years after the primary release.

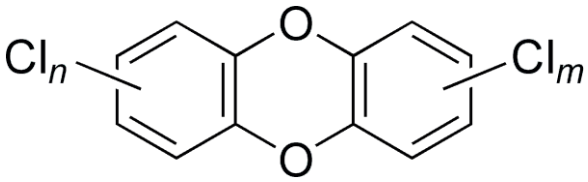


Fig. 7.12 Example of a PCDD (dioxin)

These are a type of organic hydrocarbon molecule where; two oxygen atoms are substituted to the para positions of a benzene ring with two aromatic benzene rings on either side. Chlorinated dioxins have a high stability; they have a low solubility in water and less volatility. They undergo particle formation effortlessly with air, water and soil.

Dioxins are linked to a number of negative impacts in humans, such as immune disorders, enzyme disorders and chloracne, while being probable human carcinogens. An increase in birth defects and stillbirths was seen in laboratory animals exposed to dioxins. Fish subjected to dioxin exposure died soon after the exposure ceased.

DICTIONARY

Chloracne: a skin disease similar to severe acne, caused by exposure to chlorinated chemicals.

7.13 Functional Characteristics of Polychlorinated dibenzofurans (PCDF)

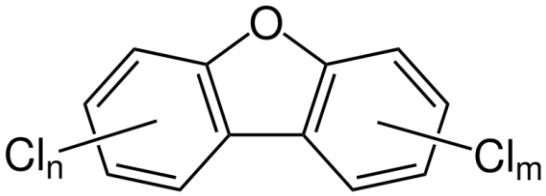


Fig. 7.13 Example of a PCDF (furan)

Furans have a structural similarity to dioxins and possess many common toxic effects like dioxins. 135 different types of dioxins exist with varying toxicity.

Dibenzofurans contain two benzene rings attached to a central furan ring. A furan is a four carbon ring structure with one oxygen atom. PCDFs contain 1- 8 chlorine atoms attached to the benzene rings of dibenzofurans. These have extremely low solubility's in water, stable for acids and alkali and withstand high temperatures.

Furans have a persistent and long existence and are probable human carcinogens. Animal products in food consumption is the main exposure route for humans. In addition, furans have been reported in breast-fed infants.

7.14 Functional Characteristics of heavy metals

Heavy metals can be defined as metals or metalloids possessing molecular weights between 63.5 and 200.6 g mol $^{-1}$ and a specific gravity/density greater than 5.0 g cm $^{-3}$ (Appenroth., 2010). However the chemical properties of heavy metals play an important role in various aspects like usage and toxicology compared to the physical properties like density. Densities of some common heavy metals are listed in Table 7.1.

Table 7.1: Density values of some common heavy metals (Baird and Cann; 2005)

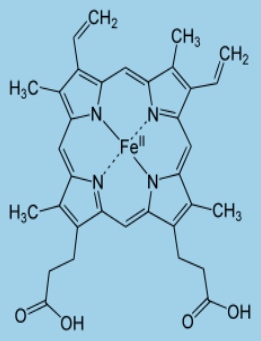
Metal	Density (g cm^{-3})
Mercury (Hg)	13.5
Lead (Pb)	11.3
Copper (Cu)	9.0
Cadmium (Cd)	8.7
Chromium (Cr)	7.2
Tin (Sn)	5.8-7.3
Nickel (Ni)	8.9
Arsenic (As)	5.8

Heavy metals are widely used in industries due to their exceptional qualities such as high degrees of ductility and low corrosiveness.

Lead, iron, cadmium, copper, zinc, chromium, arsenic, mercury are some of the heavy meals which can be found commonly in drinking water. Among these heavy metals Zn, Cu and Fe are required by plants and animals. Metals such as Cu, Zn, Fe, Mn, Mo, Ni and Co are essential micronutrients for plants while the concentrations greater than the maximum permissible levels are toxic to both flora and fauna. These essential heavy metals play a part in biochemical and physiochemical functions in both plants and animals by participating in redox reactions and by being integral parts of several enzymes. Although metals like Cu, Fe, and Zn are essential for humans as they are required by the human body in trace levels for biological functions, heavy metals like Pb, Cd, As, Hg and Cr are not reported to have any important biological functions in the human body. Toxic effects of heavy metals are due to the interference of these metals with the normal metabolic process of the human body. When these heavy metals are ingested, they are converted into their stable oxidation states ($Pb2^{+}$, $Cd^{2+,}$ As^{3+} and Hg^{2+}) in the presence of the acidic pH present in the stomach . These ions are capable of forming strong chemical bonds with biological molecules such as proteins and enzymes (Duruibe *et al*; 2007).

Furthermore, a metal ion in the body's metallo-enzyme has the ability to be substituted by another metal ion of similar size. Thus Cd^{2+} can substitute Zn^{2+} in some dehydrogenating enzymes, paving the way for cadmium toxicity.

Do you know? : Enzymes are biological catalysts which are responsible for many of the body's functions. Some enzymes have metal ions in their structure and are therefore called **metallo-enzymes.** E.g.: Haemoglobin *(structure shown below)*



8 Hazardous Wastes Management

8.1 Background

In accordance with national environmental protection legislation, the definition of a hazardous waste is *if it presents a health hazard or shows one or more of the qualities below*:

- Reactivity
- Ignitability
- Corrosivity
- Toxicity.

Each and every person has a sublime responsibility to treat waste chemical substances as potentially dangerous waste and take steps and measures to contain them in such a way to avoid the unsanctioned release to the surroundings or human exposure. Pollution prevention is defined as *the use of materials, processes or practices that limit or stop the production of pollutants or wastes at the point of generation*. Within this broad scope, it includes practices that decrease the utilization of hazardous and non-hazardous materials, energy, water, or other resources as well as enhancing practices that preserve natural resources through conservation or through the encouragement of more effective use. A current and detailed inspection of the operations must be performed at all facilities with the objective of minimalizing all forms of waste.

The following practices must be considered during hazardous waste management

- Protecting the public health and the surrounding environment.
- Reducing the potential of criminal and civil liability.
- Reducing costs of operation.
- Reducing the requirement for transportation and disposing.
- Improving participation of the whole community.

The main importance for pollution prevention is the waste hierarchy principles including source reduction, and subsequently recycling, treatment and disposal. Source reduction encompasses the usage of eco-friendly products and buying only required amounts. The life cycle of production, consumption and disposal and the role of consumption and the relevance of control and circular economy is shortly introduced in the Story of Stuff film (Annie Leonard 2007). Recycling of paper, tires, oil and other products should be done as much as possible. Treatment of waste is done through stabilizing, neutralizing and evaporating, incineration or disposal.

Disposal should obey the established hazardous waste program at the relevant college, industry or institution that ensures proper handling of wastes are and transported to a certified facility.

Upon preparation of a proper procedure, reviewing the programs, processes, and activities of the state agency is important and the accomplishment of the decrease in the amounts of toxic or hazardous chemicals, produced as wastes or released into the environment as pollutants, should be planned.

The above programs, processes, and activities should be subject to amendments, with the exception of those related to the order and usage of fuels by stationary sources, in order to decrease the amounts of toxic or hazardous chemicals produced as wastes or eradicating the release of toxic or hazardous chemicals into the environment.

8.2 Categories of Hazardous Wastes

Identification of hazardous waste is based on the fact whether the substance is a:

- Characteristic waste
    - Present on the D-list or the TCLP (Toxicity Characteristic Leaching Procedure)
- Listed waste
    - Materials explicitly recognized on either the F, K, U or P lists
- Universal waste
    - Batteries, lamps, pesticides, mercury in thermometers

Do you know? : The D, F, K, U lists referred below, belong to the **Code of Federal Regulations (CFR),** the codification of the general and permanent rules and regulations of the US government. The article concerned is Chapter 1, Title 40.

8.2.1 Characteristic Waste

(The below categories are under the D list)

- D001 –Ignitable Wastes (flashpoint value is less than 60º C) which includes oxidizers
- D002 – Corrosive Wastes (pH ≤ 2 or ≥ 12.5)
- D003 – Reactive Wastes (water reactive, typically unstable materials, cyanides & sulfides, etc)
- D004 – TCLP Wastes

8.2.2 Listed Wastes

- F-listed wastes originate from non-specific sources
    - E.g.: halogenated solvents utilized for degreasing equipment
- K-listed wastes originate from specific sources
    - E.g.: petroleum refining or pesticide manufacturing
- U-listed wastes are toxic wastes
- P-listed wastes are acutely hazardous wastes

8.2.3 Universal Wastes

- Universal wastes encompass the following items that are easily seen in the workplace
  - Batteries
  - Fluorescent lamps
  - Pesticides
  - Thermometers (containing mercury)

8.3 Determination of Hazardous Wastes

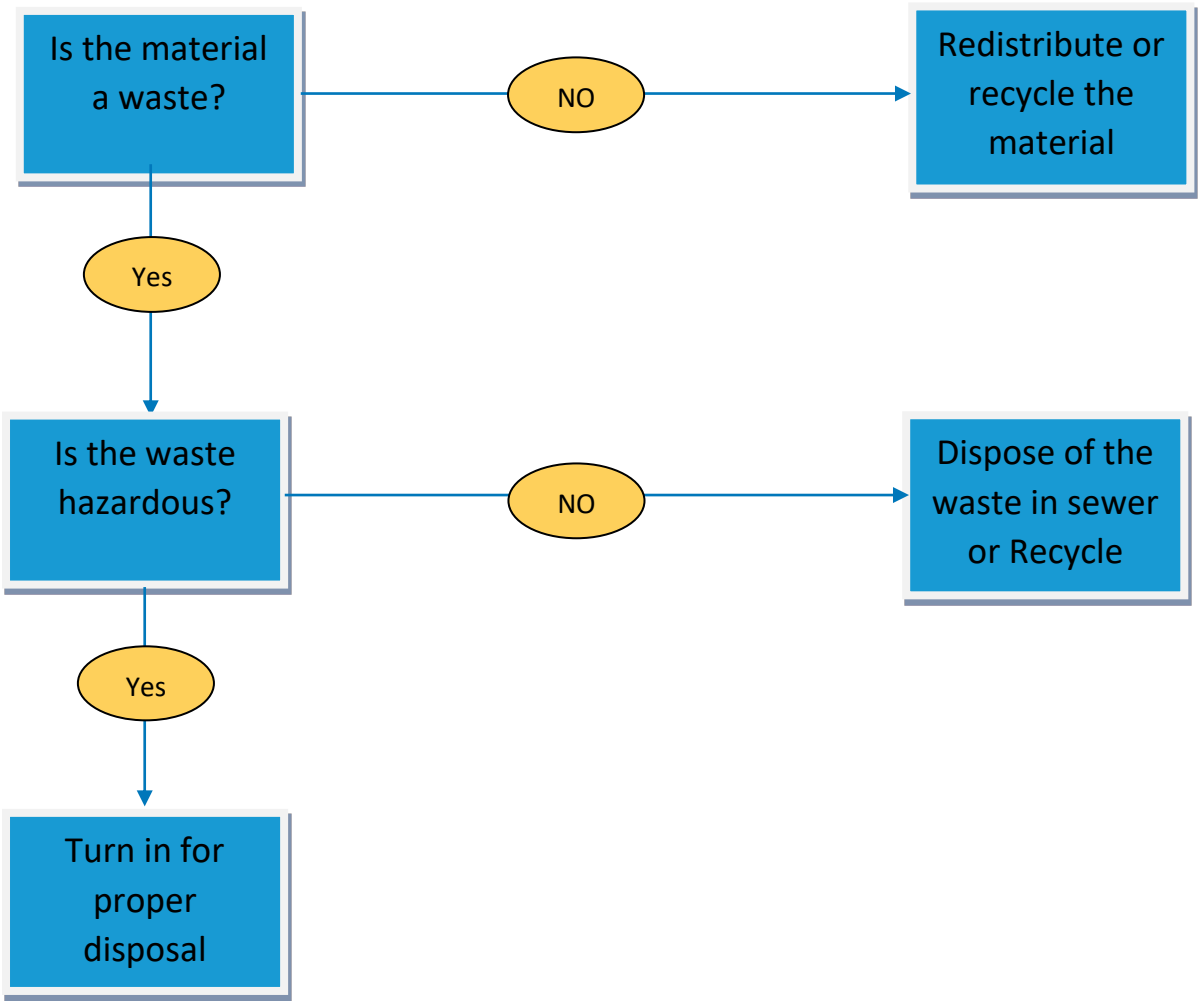


Fig. 8.1 Hazardous wastes identification process

8.4 Waste Minimization Process

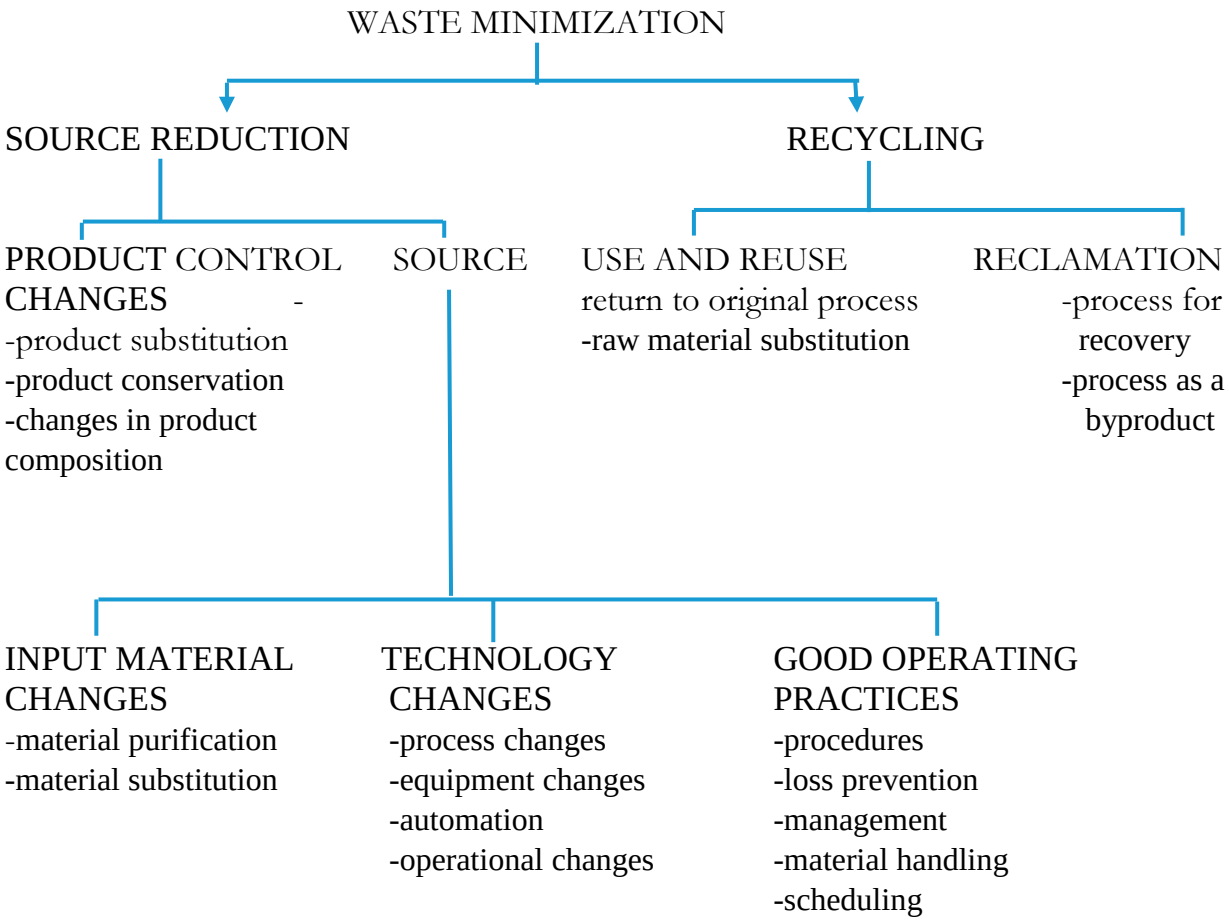


Fig. 8.2 Hazardous wastes minimization process

8.5 Source Reduction

E.g., efforts of source reduction at a school include:

Reduction of the scale of laboratory experiments

Increase of the usage of instrumentation in lab tests.

Reduction of the usage of oil-based paints

Reduction of inventories on chemical supplies.

Stopping the usage of radioactive chemicals



8.6 Recycling

Recycling is aimed at minimizing the materials coming into waste streams from the generation source. Numerous programs are created to expand and provide more productivity for the collection of recyclable materials.

DICTIONARY

Recycling is the process of converting waste materials into new materials and objects.



8.7 Pollution Prevention Assessment

- Prior planning and organization should be performed with essential elements for waste assessment such as top level management support, establishing objectives and organization of the program.
- Data should be collected on the sources and quantities of waste generation. Due to the variable nature of waste streams and volumes, the soundest source of data is a review of prior long term records. Data on waste streams may be obtained from on previous purchase orders or requisitions, hazardous waste manifests, lab pack packing lists, from sampling programs and any other probable sources. Inventories should be prepared by department to distinguish the sources, amount, types, and rates of waste generation.
- Evaluation of waste streams for possible waste minimization prospects. In setting priorities for waste streams we should evaluate the considerations for the amounts of waste generated, possibility of success for reduction, hazardous characteristics, legislation, employees' safety, economics and other qualities.
- Generation of options for additional deliberation. Source reduction and recycling options should be considered as options.
- The technical and economical evaluation must be backed by a feasibility analysis.
- If the evaluation is feasible, the program should be initiated with accompanying reviews.

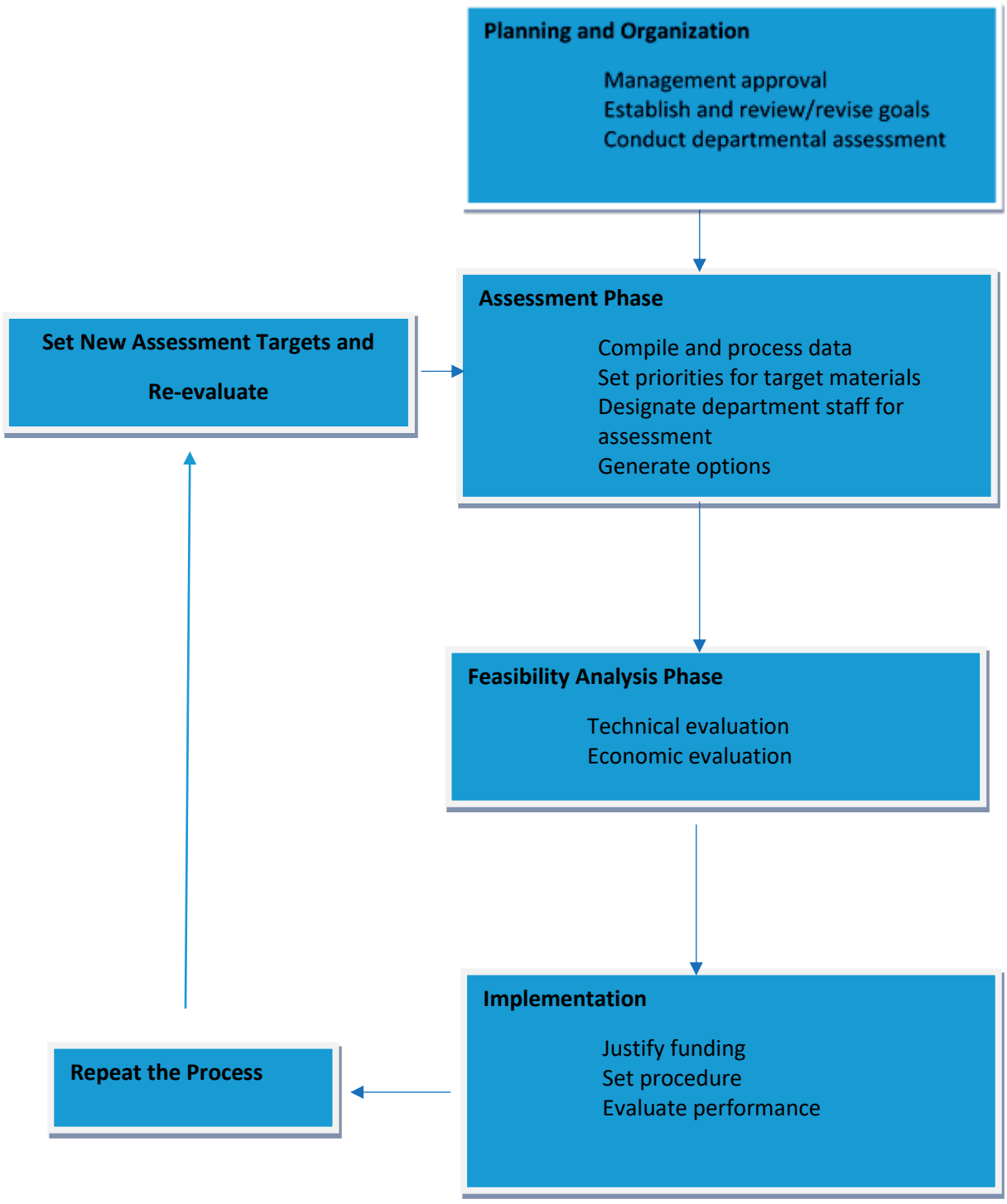


Fig. 8.3 The pollution prevention mechanism process

8.8 Waste Management Guidelines

- At least one designated person should be present as a hazardous material and waste coordinator at every location where possible hazardous materials exist who should be ordered by the administration to organize practices and protocol within the labs and/or relevant location. In addition, he/she should familiarize himself/herself with current hazardous material handling and waste disposal procedures established for the relevant institution.
- Refer the figures for the waste determination flow chart to find the material status, for Pollution Prevention Assessment, and for waste tracking.
- Prevent the combination of different types of waste because of incompatibilities or the requirement for different disposal methods.
- Keep chlorinated and non-chlorinated waste solvents in separate containers.
- All waste containers should be identified and clearly labelled as described in this document.
- Containers should be kept closed with the exception in filling or emptying stages.
- The same type of container in which the chemical was initially shipped must be used for waste storage of the chemical.
- Containers should never be filled to the brim. At least one inch of expansion space must be present.
- Corks or stoppers mustn’t be used. Properly fitting screw type lids lined with a substance that will not be subject to chemical attack by the contents should be used.
- Shock sensitive compounds should be handled with extreme care. Special handling should take place in the presence and supervision of experts.
- Wastes should be stored separately according to laboratory procedures for hazardous chemical storage. Acids should be separate from bases, and oxidizers should be separate from organics. Special flammable storage cabinets should be used for flammable chemicals, with flash points under 38°C. Containers must not be left out in the open where they may be spilled or broken accidentally. A Chemical Hygiene Plan should be present for the institution.

8.9 Tracking Mechanism of Hazardous Materials

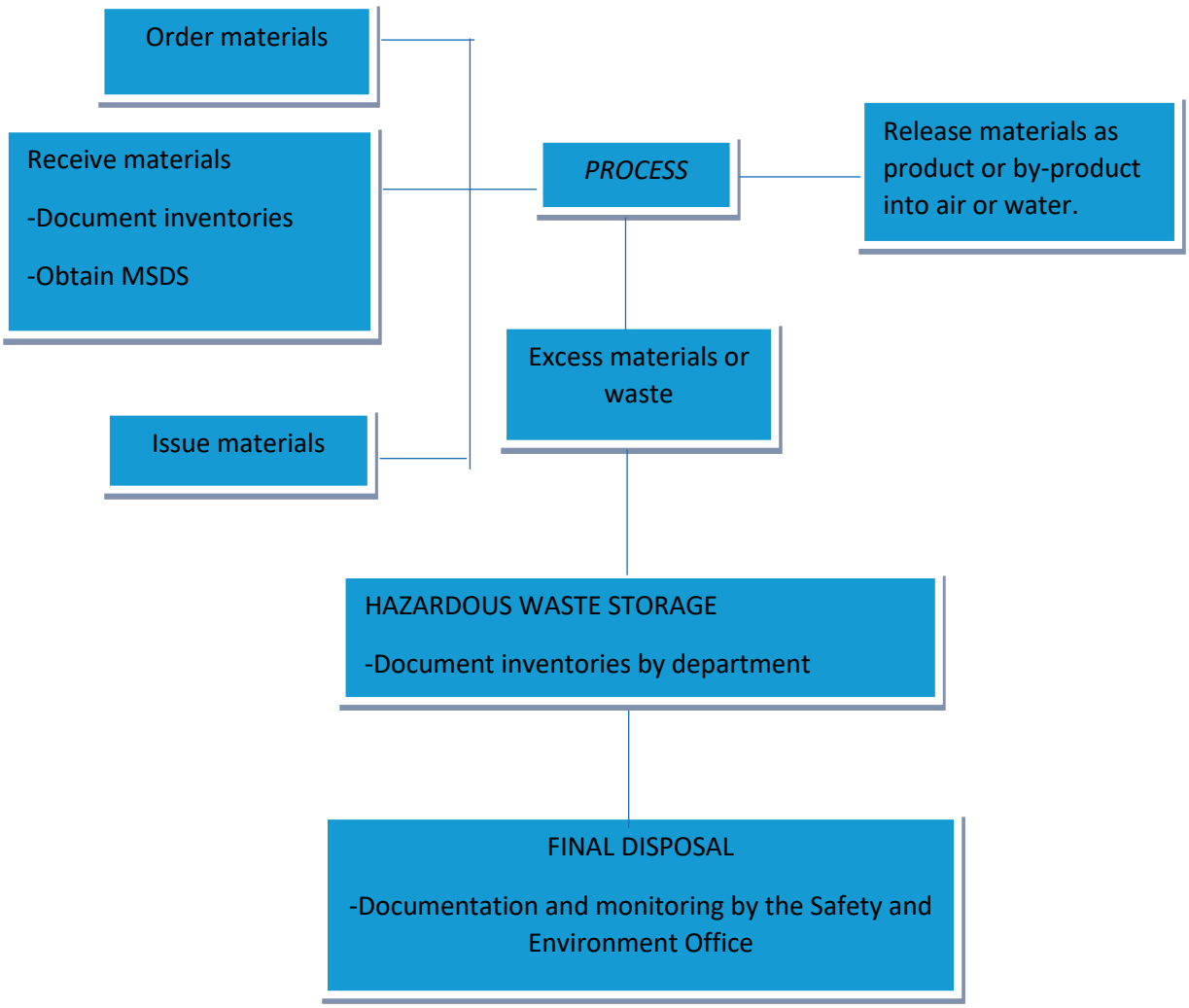


Fig. 8.4 Tracking process of hazardous wastes

8.10 Responsibilities of Stakeholders on Hazardous Wastes Management

Safety and Environment Office

- Establishment and review of operation processes yearly.
- Supervision of temporary storage facilities and the usage and disposal procedures of hazardous chemicals.
- Provision of guidance in technical and administrative aspects.

Laboratories or department managers

- Making sure that the material safety data sheets (MSDSs) are present and available.
- Provision of clear labels on each container with correct identification and safety data.
- Provision of required instructions to staff and students as need before using or handling of hazardous chemicals.

Users of potential hazardous materials

- Ensuring that all processes are done according to verified safety and health precautions which comes with the product's MSDS.
- Usage of the suitable personal protective equipment while following the instructions of the Chemical Hygiene Plan.
- All accidents, spills or unusual events in relation to the real or possible exposure or contamination resulting from toxic chemicals should be immediately reported to the relevant authorities.

8.11 Hazardous Waste Material Regulations

A Variety of institutions are established in different countries to control hazardous toxic chemicals. It is important to understand the global aspects to get a much clear picture of organizations. Some examples are,

- International agencies
    - Department of Transportation (DOT), USA
    - Occupational Safety and Health Administration (OSHA), USA
    - Environmental Protection Agency (EPA), USA
    - The European Waste policy framework (EU Waste framework)
- Sri Lankan Authorities
    - Hazardous Waste & Chemical Management Unit, Central Environment Authority
    - National Aquatic Resources Research and Development Agency (NARA)
    - Marine Environment Protection Authority (MEPA)
    - Office of the Registrar of Pesticides (ROP)

8.11.1 Department of Transportation (DOT) Regulations

DOT classifies hazardous materials into nine primary hazard classes which are divided into several subsidiary risk groups. The main classes of hazard are:

Class 1: Explosives

Class 2: Compressed Gases

Class 3: Flammable Liquids

Class 4: Flammable Solids

Class 5: Oxidizers

Class 6: Poisons and Toxics

Class 7: Radioactive materials

Class 8: Corrosives

Class 9: Miscellaneous hazardous materials that are incompatible with any other hazard class (i.e. dry ice)

USA Occupational Safety and Health Administration (OSHA) regulations

OSHA (USA) regulations comprise of the following standards:

- Hazard Communication Standard (Hazcom, Right-to-Know)
- Occupational Exposure to Hazardous Chemicals in Labs, including prerequisites for Chemical Hygiene Plans
- Respiratory Protection Standard
- Confined Space Entry Requirements
- Asbestos Standard
- Lead (Pb) Standard
- Bloodborne Pathogen Standard
- Formaldehyde, Benzene, and Methylene Chloride standards

8.11.2 US Environmental Protection Agency (USEPA) regulations

The United States Congress legislated a number of acts that the EPA uses to establish regulations to protect the environment:

- Resource Conservation Recovery Act (RCRA)
- Clean Air Act
- Clean Water Act
- Toxic Substances Control Act (TSCA)
- Emergency Planning & Community Right-to-Know Act (EPCRA)
- Comprehensive Environmental Response, Compensation and Liability Act (CERCLA)

8.11.3 The European Waste Policy Framework

The EU waste framework enhances the opportunity for waste recycling and recovery. Their waste management hierarchy includes is summarized in the Figure 8.5 below.

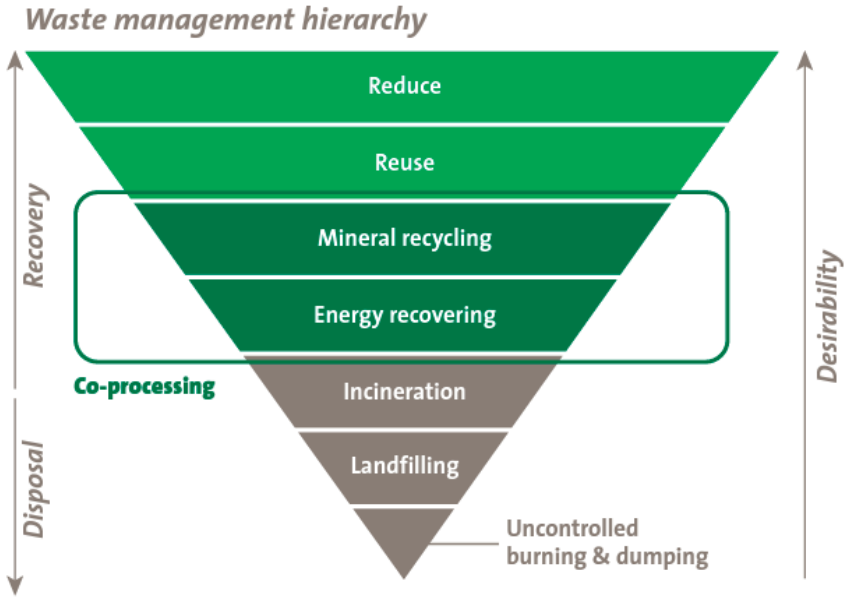


Fig. 8.5 Waste management hierarchy

Source-https://www.holcim.com/sites/holcim/files/atoms/files/lafargeholcim_co-processing_geocycle_institutional_brochure.pdf

8.11.4 Central Environmental Authority (CEA) regulations

According to the Extra-Ordinary Gazette 1534/18 dated 01.02.2008, hazardous waste have been defined as "Scheduled Waste" listed in the above gazette. Part II of the National Environmental (Protection & Quality) Regulations No 01 of 2008 describes that each individual participating in the handling of scheduled waste including the generation, collection, transport, storage, recovery or recycling and disposal of waste or the establishment of any site or facility for the disposal of "Scheduled Waste" specified in the schedule VIII of the Regulation, must acquire a license from the CEA.

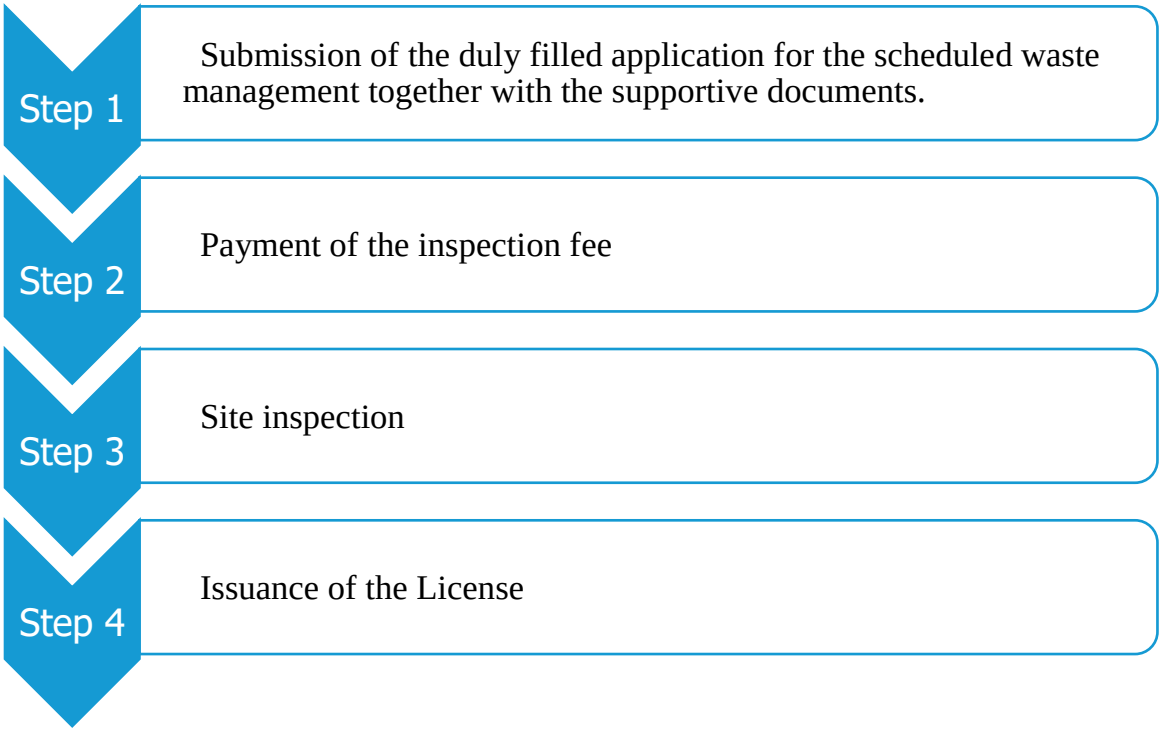


Fig. 8.6 The scheduled waste management licensing procedure

Source -http://www.cea.lk/web/en/2013-05-07-07-51-07/environmental-pollution-contorl-division/waste-management-unit?id=61

Procedure for importing waste or recycled materials

The CEA implements the national commitments on import, export and transit of waste in accordance with the Basel Convention (BC) as the state competent authority for the Basel Convention.

- Assessment if the material meant to be imported is present in the list A or list B of the Basel convention
- If it is present in the list A of the Basel convention-*reject*: If it is present in the list B - *submit an application to the Basel technical expert committee at the Central Environmental Authority*
- Submit the issue to the Basel technical expert committee at the Central Environmental Authority.
- The technical expert committee arrives at a decision which is sent to the National Coordinating Committee for the implementation of the Basel convention of the Ministry of Environment.
- Upon granting of permission, industries are permitted to import waste/ recycled chemicals/substances present in the list B of Basel convention.

- The industry will be inspected by waste management unit officers before renewal of approvals.
- The material balance must be submitted by industry owners to the Central Environmental Authority to qualify for the next renewal.

Source - http://www.cea.lk/web/en/2013-05-07-07-51-07/environmental-pollution-contorl-division/waste-management-unit?id=62

8.12 Hazardous Wastes Treatment

It is important to treat hazardous waste before disposing it to the environment. In the past few decades, there was no or less treatment for hazardous waste while disposal was prominent. Hazardous and solid waste amendments in the RCRA *(The Resource Conservation and Recovery Act)* stress on development and the use of innovative treatment technologies which results in the permanent destruction of hazardous waste or the reduction of volume mobility and toxicity of hazardous wastes. These RCRA amendments thereby restricted the land disposal of hazardous wastes.

Treatment technologies of hazardous wastes can be placed into the following categories:

- Physical
- Chemical
- Biological
- Thermal
- Stabilization

8.12.1 Physical Treatment

Physical Treatment processes are further divided in to

- sedimentation,
- adsorption,
- aeration
- other physical processes.

8.12.1.1 Sedimentation

Solids are separated from liquid with gravity settling and natural flotation (also spelled floatation). In the sedimentation and clarification tank, settled solids are collected at the bottom of the tank as sludge. A skimming device is used to remove solids that naturally float to the surface. The flotation process can be enhanced by the introduction of fine air bubbles to the waste stream. Separated sludge is concentrated with evaporation, centrifugation or filtration.

8.12.1.2 Adsorption

Adsorption can be used to remove small concentrations of dissolved hazardous substances which are not settled. It is a physical adhesion of a chemical on the surface of a solid. The extent of the surface area is responsible for the adsorption effectiveness. Granular activated carbon (GAC) is the commonly used absorbent material for water treatment.

8.12.1.3 Aeration

If the chemicals have volatile properties, aeration can be used eliminate the substance from the solution. Normally for this process, air is used, but in some cases, steam is also used. The contaminated water is sprayed downward through the packing material while in the meantime, air is blown upward. It is possible to remove volatile and non-volatile compounds by combining air stripping with GAC.

8.12.1.4 Other Physical Processes

Reverse osmosis, *ion exchange* and *electro-dialysis* can be considered as the other treatment methods for hazardous waste treatment. In reverse-osmosis, devices use pressure to force contaminated water against the semi-permeable membrane that acts as a filter. Ion exchange is a process to remove ions from waste water by exchanging ions associated with a special ion exchange resin. This method is commonly used to remove toxic metal ions from the solution. An ion selective membrane and an electric field are used in the electro-dialysis process which enhances the separation of anions and cations in the solution. Metal salts from planting rinses can be removed using this method.

Do you know? : Reverse osmosis is currently even used to produce drinking water from seawater in the Middle East!



8.12.2 Chemical treatment

8.12.2.1 Neutralization

Hazardous waste which compose of chemicals which are corrosive or having a pH less than 2 or more than 12.5 should be chemically neutralized. Slaked lime ($Ca(OH)_2$) is normally used to neutralize acidic wastes in a continuously stirred chemical reactor. Alkaline wastewaters are neutralized by adding acids or by bubbling CO_2 gas.

8.12.2.2 Chemical Precipitation

It is important to remove undesirable substances from wastewater. As an example, removal of heavy metals can be carried out using chemical precipitation. The solubility of toxic waste can be decreased by adjusting pH to induce precipitation. The final precipitate is removed using settling and filtration.

8.12.2.3 Chemical Reduction-Oxidation

This is a very important treatment method for hazardous waste treatment. Both oxidation and reduction occur in same direction.

Oxidation of cyanide waste is a common example for this. Cyanide is converted to the less toxic cyanate compound using alkaline chlorination. Further chlorination oxidizes cyanate to CO_2 and NO_2.

$$NaCN + Cl_2 + 2NaOH \longrightarrow NaCNO + 2NaCl + H_2O$$

$$2NaCNO + 3Cl_2 + 4\ NaOH \longrightarrow 2CO_2 + N_2 + 6NaCl + 2H_2O$$

Waste that includes benzene, phenol, organics, cyanides, As, Mn, Fe can be treated using this method. (US EPA 1988a).

8.12.2.4 Advanced Oxidation Processes (AOPs) and Semiconductor Photocatalytic Processes (SPCPs)

Among the various pollutant treatment methods in the literature, the aforementioned methods are promising technologies for the complete mineralization of organic pollutants with the generation of carbon dioxide, water and mineral acids. The destruction process is caused by Reactive Oxygen Species (ROSs)

DICTIONARY

Fe(0) refers to zerovalent iron (ZVI) which is basically its elemental form. It is used in permeable reactive barrier (PRB) treatment methods which filters out contaminants in groundwater.

such as the superoxide radical anion (($O_2^{\cdot -}$)), hydroxyl radical ($HO^{\cdot}$) which are extremely reactive attacking chemical species.

ROSs are formed by the sequential reduction of molecular oxygen through the addition of electrons. In AOPs, methods like UV/H_2O_2, UV/O_3, UV/H_2O_2 /O_3, UV/Fe(0) could generate ROSs. In recent years, particular attention has been focused on photocatalytic degradation processes, because of its higher efficiency, stability and low-cost.

8.12.3 Biological Treatment

8.12.3.1 Aqueous Waste Treatment

Leachate from hazardous waste landfills is treated after chemical and physical treatment processes, because it is required to carefully control the characteristics of waste which reach the biological compartment of the facility. In addition, the waste should be adjusted to the right pH and nutrient supply should be provided as it is important for microorganisms in the biological treatment step.

The sludge generated from the system should be dewatered and disposed, according to RCRA regulations.

8.12.3.2 In-situ Biodegradation

Pumping out ground water and subsequent treatment is one of the ways to clean contaminated aquifers. Treated water can be reused or disposed of to the environment. In this process, bacteria is used to degrade organic compounds in the soil and ground water at the particular site. The second approach of in-situ bio degradation is altering the underground microbial population by seeding new microorganisms that have the ability to degrade pollutants effectively. This is a very new technique to treat chlorinated solvents such as trichloroethylene (TCE), tetrachloroethylene (PCE), and 1,2-dichloroethyelene.

8.12.4 Waste Incineration

This method is a widely accepted method for waste treatment, if Best Available Technology is used (European Commission 2006) and if the ashes are disposed safely which often is a problem in developing countries with associated pollution (Petrlik and Bell 2017). Many types of hazardous wastes can be destroyed by incineration. Incineration processes are effective with organic waste, soils, gases, liquids, slurries and sludge. However it is ineffective against heavy metals as they aren't destroyed. In fact, the carcinogenicity of chromium is increased by incineration. In addition, carcinogens, mutagens, teratogens and pathological wastes can be completely detoxified in incinerators. There are two principal designs of hazardous waste

incinerators: 1. Rotary kiln incinerators and 2. Liquid injection incinerators. Rotary kiln incinerators can handle gases, liquids, sludge and solids of all sorts. Liquid injection incinerators are used only for gases, liquids and slurries which are thin enough to be pumped through the atomizing nozzle. Cement kilns are also used for a range of hazardous wastes (http://www.coprocem.org/Guidelines). This has shown promise in Sri Lanka as well although not used routinely (Karstensen et al., 2010). In addition, there are other types of incinerators used in the EU such as fluidized beds, pyrolysis and gasification systems, and combination processes.

8.12.5 Land Disposal

Landfills, surface impoundments, underground injection wells and waste piles are commonly used land disposal techniques. In developed countries, such as the United States, specially designed landfills are placed for hazardous waste disposal. About 5% of hazardous waste are disposed in this method. About 35% of hazardous waste are disposed in surface impoundments such as lagoons, ponds pits and basins. It is important to consider about poorly engineered and monitored waste disposal sites, and the remediation of older sites which have leaked toxic chemicals into the ground water and soil. Therefore it is not allowed in most European countries.

8.12.5.1 Landfills

Hazardous waste landfills are currently designed as a modular series of three dimensional control cells. Wastes are segregated and compatible waste is disposed together. At the end of each working day, the dumped waste are covered with a soil layer. The landfill should include monitoring facilities.

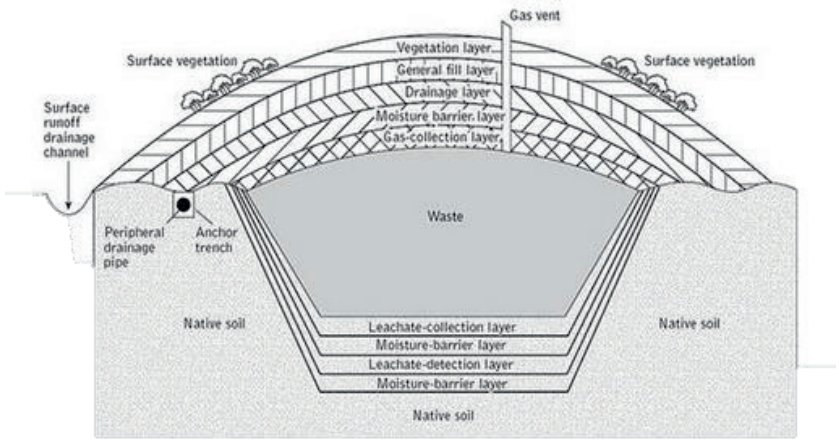


Fig 8.7 Cross section of hazardous waste landfills.

8.12.5.2 Surface Impoundments

Surface impoundments are excavated areas which are used to store liquid hazardous waste. These techniques are popular due to low cost while treatment can be done to the waste during storage. Neutralization, precipitation, settling, and biodegradation are the commonly used treatment technologies in surface impoundments.

8.12.5.3 Underground Injection

Hazardous waste is injected underground through deep injection wells. It is essential to make sure that the underground drinking water reserves must not be contaminated. Normally, injection wells are required to be extended below the lowermost point of the formation of underground water sources. The typical depth of injection wells is more than 700m below the surface.

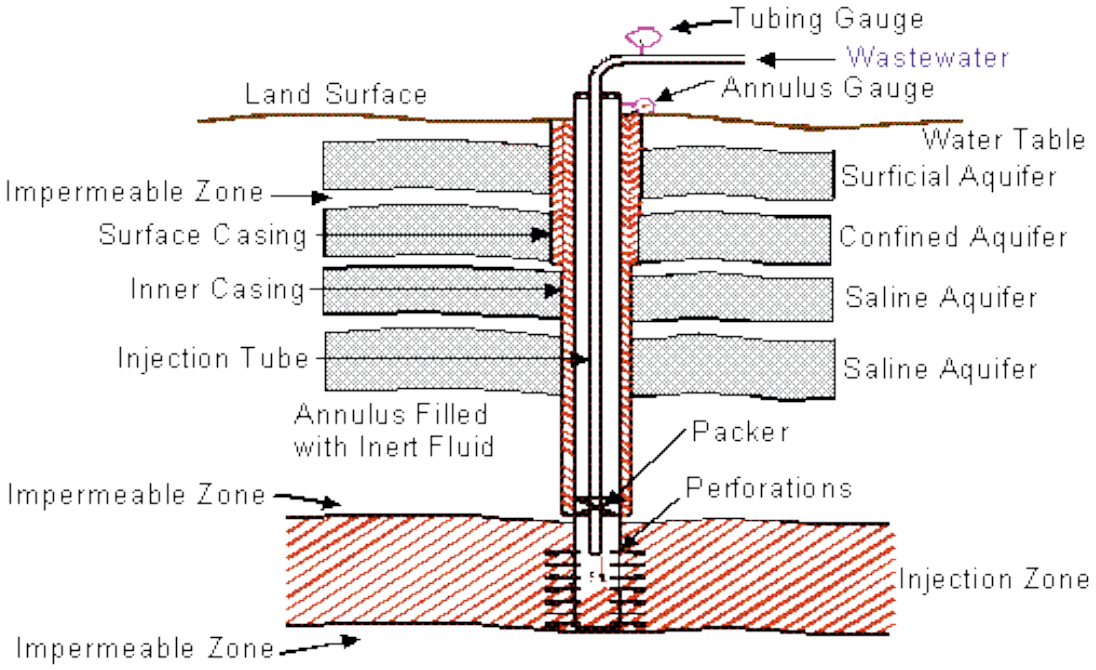


Fig. 8.8 A cross section of hazardous waste injection well

Source - http://web.deu.edu.tr/atiksu/ana58/deepwell.html

9 Toxicology

9.1 Characteristics

PBTs present an immense threat to the environment since they may accumulate in predators due to bioaccumulation *(see Chapter 3).* Higher concentrations of PBTs have posed a concern to several top chain consumers such as ospreys and peregrine falcon populations. After governmental bans of chemicals such as DDT, several predator populations such as bald eagles have begun to resurface in North America.

The increased persistence and high concentrations may amplify the toxic effects of PBTs which may include mutagenic damage to DNA, cancer, neurological toxicity, reproductive toxicity, developmental toxicity, or immune system damage. Endocrine disrupting chemicals (EDC) are an immense concern among toxic chemicals. Diamanti-Kandarakis et al (2009) states that polychlorinated biphenyls (PCBs), polybrominated biphenyls (PBBs), dioxins and DDT may disrupt the receptor sites of hormones which may inhibit or distort physiological responses thus setting homeostasis out of balance. Endocrine-disrupting chemicals (EDCs) were originally thought to exert actions primarily through nuclear hormone receptors, including estrogen receptors (ERs), androgen receptors (ARs), progesterone receptors, thyroid receptors (TRs), and retinoid receptors, but recent studies have shown that they can disrupt essential receptors such as serotonin, dopamine and epinephrine. They may result in altered reproductive function in males and females, increased incidence of breast cancer, abnormal growth patterns and neurodevelopmental delays in children, as well as changes in immune function. (WHO, 2018)

The main properties of PBTs that enhance their effects are their persistence, bioaccumulative nature and high toxicity. Usually chemicals that contain halogen atoms enable a resistance to degradation to environmental factors such as sunlight, chemicals or bacteria. This also provides the ability to resist breakdown by biological metabolic activities in human and animal bodies. Their volatility when combined with persistence may enable them to travel to far distances from their site of origin (Safer Chemicals, Healthy Families. 2018).

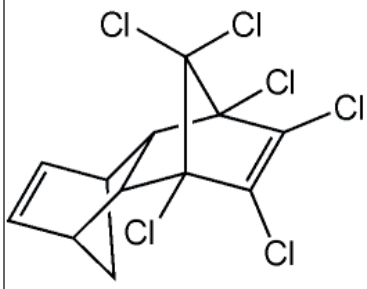
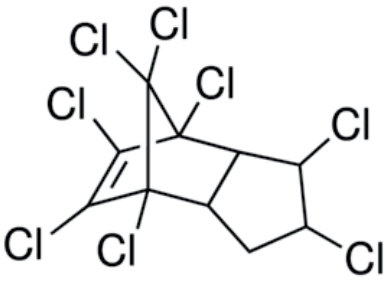
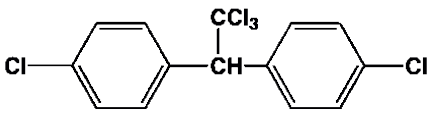
Many of these chemicals are soluble in fats, therefore cannot be easily removed by hydrophilic means in excretion. Therefore, they tend to accumulate in bodies to high concentrations in adipose tissue. This explains the reason for an elevated concentration of PBTs in fat-rich breast milk (LaKind 2004). PBTs may also be found in the yellow marrow of bones, muscles and even in the brain of the animals (Safer Chemicals, Healthy Families. 2018).

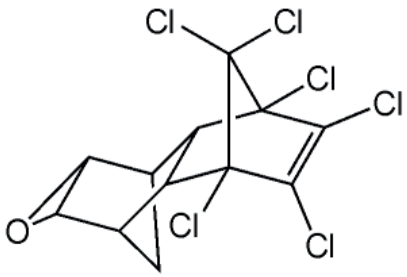
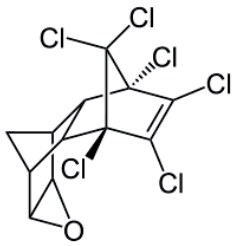
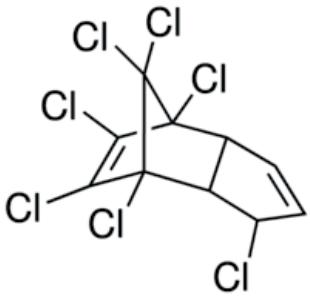
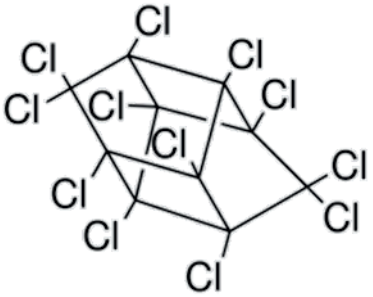
9.2 Toxicology

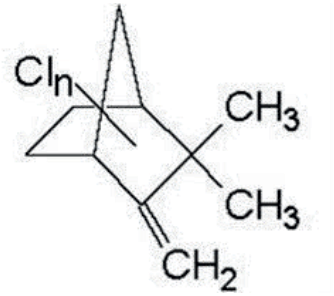
9.2.1 The Effects of PBT Pesticides

In order to prevent and treat the adverse effects of PBTs on the environment, the toxicological effects on living organisms should be analyzed. Table 9.1 depicts the health effects of different PBTs which are found in pesticides on humans & animals known so far.

Table 9.1: PBTs pesticides and their effects (Source: ATSDR, 2011)

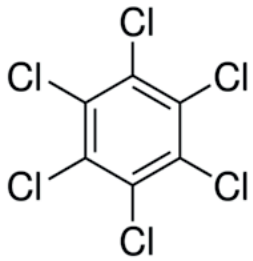
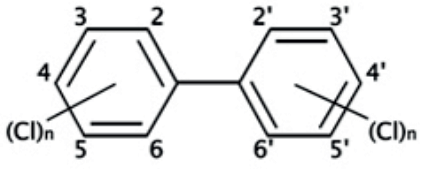
PBT pesticide	Effects
Aldrin 	• Symptoms include dizziness, headache, nausea, general discomfort and vomiting, followed by muscle twitching, myoclonic jerks, and convulsions. • Affects endocrine, hepatic, immunological (immune system) and neurological systems. • Found in birds, invertebrates and soil. • Human lethal dose is 5g.
Chlordane 	• Symptoms include mild dizziness, weakness and headaches. • Affects development systems, hepatic and neurological systems. • Chlordane is moderately toxic to birds, highly toxic to fish, and toxic to bees • Bioconcentrates with a half-life of one year.
DDT **(Dichlorodiphenyltrichloroethan**  **DDT**	• A possible human carcinogen. • Blocks androgenic hormone receptors. • Affects developmental, endocrine, liver, nervous system and reproductive systems. • Highly toxic to fish and acutely toxic to birds.

Dieldrin  	● May cause liver and breast cancer, and found in breast milk. ● Affects endocrine, hepatic, immunological (immune system) and neurological systems. ● Bioconcentration factors of 12,500 and 13,300 have been reported for guppies and sculpin ● Half-life in soil is 5 years.
Endrin  	No evidence regarding carcinogenicity. ● May cause convulsions or seizures. ● Affects the nervous system. ● Persist in soil for up to 12 years (long half-life). ● Highly toxic to fish (e.g. early stage hatching of sheepshead minnows).
Hepatachlor  	● Affects the liver and nervous system with symptoms such as tremors and convulsions. ● Classified as a probable carcinogen. ● Bio-concentrates in the fat of organisms. ● Metabolized in animals to heptachlor epoxide which has similar toxicity. ● Responsible for the decline of several wild bird populations including Canadian Geese and American Kestrels.
Mirex  	● Anticipated to be a human carcinogen. ● Affects kidneys, reproductive and nervous systems. ● Rats subjected to poisoning show lower litter sizes. ● Bio-accumulates and bio-magnifies with a half-life of 10 years. ● Toxic to several plant species, fish and crustaceans.

Toxaphene  	● Possibility of carcinogenicity. ● Affects endocrine system and liver. Increases liver size and weight. ● Persist for long periods in the soil (50% up to 12 years). ● Highly toxic to fish (e.g. brook trout – weight loss and reduced egg viability).

9.2.2 The Effects of PBT Industrial Chemicals

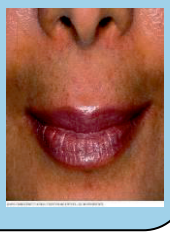
Table 9.2: PBTs industrial chemicals and their effects (Source: ATSDR, 2011)

PBT industrial chemical	Health Impacts
Hexachlorobenzene (HCB)  	● Affects developmental systems, liver and reproductive systems. ● Symptoms including photosensitive skin lesions, hyperpigmentation, hirsutism, severe weakness, porphyrinuria, and debilitation. ● Bio-concentrates in the fat of living organisms. ● Toxicity in aquatic organisms is comparatively low.
Polychlorinated biphenyls (PCB)  	● Affects skin, developmental organ systems, endocrine (glands and hormones), liver, immune system and nervous system. ● Signs and symptoms of exposure include enlargement and hyper secretion of the tarsal glands of the eyes, swelling of the eyelids, and pigmentation of the nails and mucous membranes, occasionally associated with fatigue, nausea and vomiting. ● Probability of being carcinogenic. ● Toxic to fish, lethal at higher doses. ● Spawning failures at lower doses. ● Major damage – reproductive failure and suppression of immune system in animals.

Have a look at this video about the impacts of toxins on the developing brain. (Video courtesy of IPEN International POPs Elimination Network)

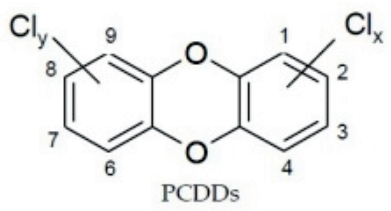
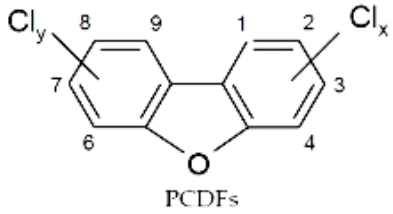
https://www.youtube.com/watch?v=E6KoMAbz1Bw

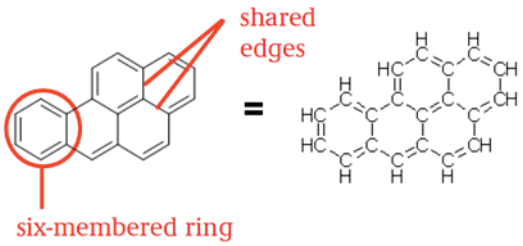
Do you know? : Hirsutism is a condition that results in growth of facial hair in females similar to males!



9.2.3 The Effects of PBT Unintentional By-products

Table 9.3: PBTs unintended byproducts and their effects (Source: ATSDR, 2011)

PBT by-product	Health Impacts
Polychlorinated dibenzo-p-dioxins (PCDD)  PCDDs	• Affects skin, developmental organ systems, immune system and reproductive system. • The main persistent effect in humans is chloracne (an acne-like eruption of blackheads, cysts, and pustules) • In addition other health effects include peripheral neuropathies, fatigue, depression and personality changes.
Polychlorinated dibenzofurans (PCDF)  PCDFs	• Known to be teratogens (cause defects in physiological development), mutagens (may cause mutations), and suspected human carcinogens. • Bio-accumulates in tissues rich in lipids. • Bio-concentrates through food chains due to high fat solubility. • Bio-magnifies in marine food chains. • Acneiform eruption, dermal pigmentation and increased eye discharge were observed during a case of exposure in Japan. (Masuda 2001)

Polycyclic Aromatic Hydrocarbons (PAH) 	• Include examples such as Benz[a]-anthracene, Benzo[a]-pyrene, Benzo[e]-pyrene, Chrysene, Dibenz[a,h]-anthracene, Naphthaline. • The majority are carcinogens. • Affects skin, liver and immune systems. • PAHs in cigarette smoke may cause cardiovascular disease. • Chrysene and naphthalene are very toxic to aquatic organisms. • The effects are mostly long lasting.

9.2.4 The Effects due to PBT Heavy Metals

Table 9.4: PBT heavy metals and their effects. (Mayo Clinic, 2018).

PBT heavy metal	Health Impact
Lead 	• Affects cardiovascular system, developmental systems, gastrointestinal (digestive), hematological (blood forming), musculoskeletal (muscles and skeleton), neurological (nervous system), ocular (eyes), renal (urinary system or kidneys), reproductive systems. • Potent child neuro-toxicant. • Possibly carcinogenic to humans. • Symptoms of lead poisoning include developmental delay, learning difficulties, irritability, loss of appetite, weight loss, sluggishness and fatigue.

Mercury (includes organic and inorganic) 	• Affects developmental organ systems, digestive systems, neurological (nervous system), ocular (eyes) and renal (urinary system or kidneys) system. • causes developmental neurotoxicity; children most susceptible • Caused Minamata disease in Japan in 1950s. • Symptoms include muscle weakness, poor coordination, rashes and convulsions.
Cadmium 	• Affects cardiovascular system, developmental organs, gastrointestinal (digestive), neurological (nervous system), renal (urinary system or kidneys), reproductive (producing children) and respiratory system. • Lung carcinogen • Caused Itai-itai disease in Japan in 1912, with symptoms of severe pain in spine and joints.
Arsenic 	• Affects skin, digestive system, liver, nervous system and respiratory system. • Confirmed carcinogenicity to humans. • Acute symptoms may include vomiting, diarrhea with blood and encephalopathy. • Chronic symptoms may include heart disease, thickening of skin and abdominal Do you know? Arsenic poisoning was a preferred murder method during the Middle Ages in Italy because its symptoms were very similar to cholera

9.3 Detoxification

The body is a complex machine. For the coordination, of this machine, we have two organ systems namely the nervous system and the endocrine system for better homeostasis. The nervous system relies on electrical signals transmitted as nerve impulses through neurons. The endocrine system composes of organic molecules called hormones/hormonoids, which are secreted by endocrine glands in low concentration and distributed through the blood stream to target organs, which may stimulate a physiological response. Even in the nervous system, chemical messengers are used to transmit signals between the gaps of individual neurons (nerve cells) called synapses. The qualitative identity of a chemical is recognized by a special receptor at a target organ, and it allows the organ to respond to the chemical. Therefore, most of the chemicals play an important part in the body's communication system. Therefore, an imbalance (an excess or deficiency) or introduction of certain new chemicals may cause a disruption or disturbance in the body's coordination system. They may inhibit the body's vital function e.g.: neurotoxins, haemotoxins, enterotoxins, reproductive toxins, and cytotoxins.

> **DICTIONARY**
>
> **Homeostasis** is defined as the maintenance of a constant internal environment within the body.

Chemicals are taken up by the body mainly by ingestion through the digestive system, which are absorbed through the small intestine and enter into the bloodstream. They may also enter through inhalation and enter the respiratory system and accumulate in the alveoli in lungs or diffuse into blood capillaries and can be distributed throughout the body with the blood circulation. In addition, they may also diffuse through the skin into blood upon skin contact. To maintain the proper homeostasis and optimal function of the bodily systems, detoxification processes are essential for an organism.

Detoxification takes place primarily in the liver. Hepatocytes (liver cells) contain a large number of organelles called peroxisomes, which oxidize toxins. The main stages of *in vivo* detoxification are divided into three.

Phase 1: The human cell membrane acts as the outer boundary of the cell and is mainly composed of lipids (phospholipid bilayer). Lipophilic toxins can easily breach this barrier and engage in unregulated transport. Therefore, using an enzyme called cytochrome P450s (CYP450) many of these toxins are made water soluble, so the entry and exit of these toxins can be regulated, by proteins in the cell membrane acting as gates.

Phase 2: Using another type of enzyme, some of the toxins are made water soluble even further and their toxicity is decreased. Several chemical groups such as sulfate, glucuronic acid and glycine are added to the toxin molecule.

Phase 3: The toxic elements are transported out of the cells and introduced to excretion pathways. Toxins may be ejected in liver through bile or may be filtered in the kidney and released through urine.

Toxification

Sometimes the cytochrome P450 (CYP450) enzymes in Phase 1 may convert a toxin into a more lethal form in its chemical reactions. These may be hepatotoxic and may damage the liver. Paracetamol (acetaminophen) if taken in high doses may undergo the Toxification process stated above and cause liver damage. Another example is methanol which may be converted to the more toxic forms of formaldehyde or formic acid.

Toxicokinetics refers to *the study of absorption, distribution, metabolism/biotransformation, and excretion (ADME) of toxicants/xenobiotics in relation to time.* (Gupta 2016)

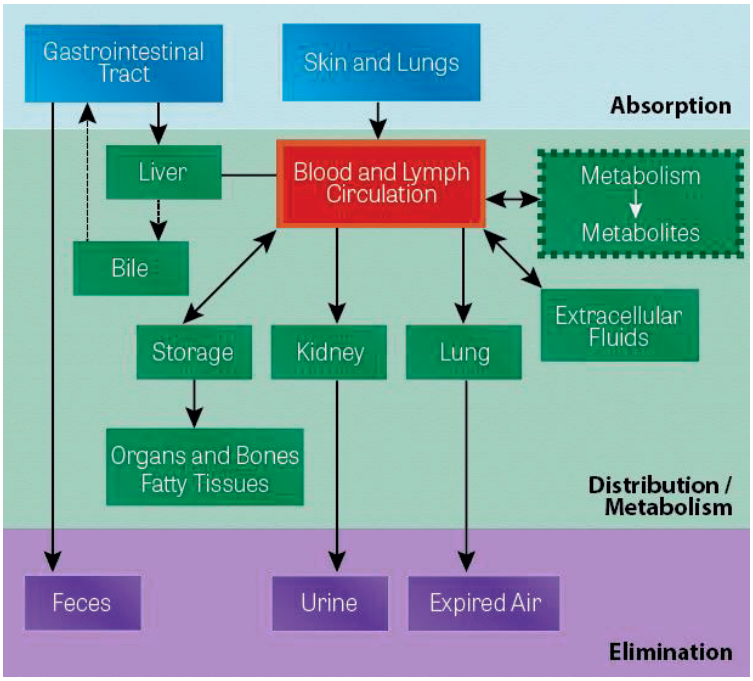


Fig. 9.1 Absorption, distribution, metabolism and elimination pathways (adapted from the US National Library of Medicine)

Toxicologists use different mathematical models called physiological toxicokinetic models to describe and predict the behavior of a toxin in an animal body. Various absorption and transport equations are used to build up a simulation of the path of a toxicant within the body. This may be used to predict for example, what organs which a chemical may enter e.g. liver, fat deposits and whether or not the chemical is expected to be metabolized or excreted and at what rate. This helps in analyzing the effects of the toxin on the body.

DICTIONARY

Xenobiotics are defined as chemical substances found within an organism that are not naturally produced or expected to be present within the organism.

Compartmental models describe toxicant movements between compartments, which may or may not have a physiologic or anatomic meaning. The toxicant enters into a compartment according to an uptake rate coefficient and exits according to an elimination rate coefficient (Gibaldi and Perrier, 1982). The compartments/organs are divided by a connective tissue such as blood. The organs have been grouped into compartments using the criteria of similar blood perfusion rate and tissue composition. Commonly, the PBTK (physiologically based toxicokinetic model) structure only includes the organs or tissues necessary to describe the important features of ADME (Absorption, distribution, metabolism and elimination) processes of the chemical of interest and its metabolites, and the target tissues in which toxicity may arise (Gretch et al 2016). Equilibriums between tissue fluid, blood and organs are obtained from previous studies.

DICTIONARY

in vivo means, literally, "in the living." In biochemistry it indicates that an experiment is being done in conditions that precisely mirror those existing in nature, usually within a natural organism.

in vitro, in contrast, means, literally, "in glass," or "in a test tube." It indicates an experiment carried out in an artificial environment, usually conditions that are intentionally simplified

in silico means performed on a computer or via computer simulation.

A large number of information is required to present an accurate simulation to present a model. The information can be divided into two types as substance related which includes anatomical data such as organ volume, physiological data such as cardiac output and biochemical data such as enzyme concentration. Substance dependent parameters are the interactions between blood and the chemical under observation. In-vitro and in-vivo experiments are used in calibration.

Biotransformation is a frequently seen stage in toxicokinetics. It is defined as *the modification of a substance, typically a drug, within the body.* Though biotransformation is seen majorly in food nutrients, with respect to toxins, it overlaps with detoxification. However not all biotransformation processes are detoxification processes. It is very important as discussed earlier, as lipophilic toxic chemicals are transformed/ converted to hydrophilic less toxic molecules which may be easily removed by active secretion to nephrons in kidney, or passed into bile which is thereafter secreted through feces.

Usually in the phase 1 reactions described above in detoxification, toxic drugs are subjected to biochemical reactions such as oxidation, reduction and hydrolysis. Its activity is usually decreased but has a possibility of becoming more active as well, while being converted to a water-soluble form by increasing its polarity. Phase 2 reactions conjugate different chemical groups to increase the molecular weight and decrease the toxicity. Within cells, enzymes within the endoplasmic reticulum usually catalyze reactions. Oxidation is typically done by peroxisome organelles while reduction involves co-enzymes such as NADPH.

9.4 Behavioural Toxicology

Behavioural toxicology is basically *the study of chemical toxicants and their influence on brain functions.* Brain functions being a part of the coordination system, utilizes chemicals such as serotonin and dopamine. Therefore likewise certain chemicals can cause an adverse effect to brain function. For example, the Minamata disaster which was happened in Japan in the year 1956 caused many neurological damages such as coma and loss of vision for many years afterwards. Exposure to PBTs for fetuses while in the uterus may cause disabilities in the child after birth such as learning disabilities due to the genetic mutations. Many chemicals may be ingested by the mother and cross to the fetus through the placenta breaching the placental barrier.

Needleman (1995) stated that children subjected to lead poisoning at silent (very minor physiological concentrations) doses show deficits in psychological function; these include intelligence, perception, attention, language function, and perhaps social adjustment. Organophosphate and carbamate pesticides are known to inhibit an enzyme called acetylcholineesterase which is essential for the transmission of nerve impulses. Old houses bearing lead have been known to present adverse effects to their occupants.

Do you know? : A classic example of the effect on chemicals on the brain is intoxication of a drinker of alcohol!

Scott et al (2004) reviewed the behavior of fish in lakes subjected to pollution and observed that several behavior changes were seen in the areas of responses to chemical signals of predation, responses to visual stimuli of predators, locomotor behavior in escaping predators, schooling behavior (group behavior) and several changes in reproduction including spawning sites, nest building and courtship mechanisms. The publication states that this may be due to chemoreceptor stimulation with endocrine disruptive heavy metals such as cadmium, nickel and mercury. Brain neurotransmitter levels may also be disrupted by certain toxicant exposures. Brain serotonin and/or dopamine levels were reduced by copper mercury or lindane exposure in several different fish species, while in contrast serotonin and norepinephrine increased after lead exposure in fathead minnows.

9.5 Assessment of the Toxicity of PBTs

For preventive measures and remedial actions, it is important to analyze and assess the potential toxicity of PBTs. There are two main methods of assessment used in toxicology assessments namely, *in vitro* bioassays and *in vivo* bioassays.

9.5.1 *In vitro* Bioassays

DICTIONARY

An assay is an investigative (analytic) procedure in biology for qualitatively assessing or quantitatively measuring the presence, amount, or functional activity of a sample.

Any method indicating *an experiment carried out in an artificial environment, usually conditions that are intentionally simplified* can be defined as an *in vitro* assay. Animal cell and tissue culture based bioassays have been used to mimic the *in vivo* condition effectively and other than that, whole organisms like brine shrimps were also traditionally used to assess the various toxic effects of chemical compounds. In animal cell cultures, primary cells (cells that are harvested from fresh tissues) or cell lines (commercially available continuously cultured cells) grown in culture media that contain water, essential nutrients like sucrose, vitamins, growth substances, buffers and gases. These cultured cells can be treated with different doses of toxicants and then further analysis can be performed for the effects on cell viability, proliferation, DNA damage and in-detail cell signaling pathways as well.

Depending on the area on analysis and the procedure, in vitro methods can be categorized further.

9.5.1.1 Genotoxicity Assessment

Genotoxicity testing includes the measurement of DNA primary damage that can be repaired and is therefore reversible, as well as the detection of stable and irreversible damage (i.e. gene mutations and chromosome aberrations) that is transmissible to the next generation when it occurs in germ cells, and the perturbation (deviation) in mechanisms involved in the preservation of the integrity of the genome.

In vitro grown cells treated with the chemicals can be tested using molecular biological tools such as gene expression analysis using Polymerase Chain Reaction (PCR), micro array, DNA sequencing and protein analysis etc.

9.5.1.2 Cytotoxicity Assessment

Cytotoxicity consists of damage to metabolic activities of cells which may result in cell death. The cells grown in *in vitro* conditions are analyzed for measures of cytotoxicity under the following parameters.

Measurements of the metabolic state -	ATP concentration Neutral red–lysosomal sequestering Tetrazolium dye reduction Calcein AM cleavage Direct measurement (Cytosensor microphysiometer)
Measurements of membrane integrity-	Trypan blue, calcein AM, or propidium iodide uptake “Live/dead” nuclear stains Cytoplasmic enzyme release (LDH)

The above characteristics of metabolism and membrane integrity are definite characteristics of living cells. A final conclusion is taken by measuring the number of dead cells in an assay.

9.5.1.3 Safety in *in vitro* Methods

Proper biosafety procedures have to be followed in using *in vitro* cell culture based models and specially designed laboratories are a must. Precautions in a tissue/cell culture laboratory using human tissue can focus on:

• Concerns with human pathogens such as Hepatitis B, HIV, and other potentially unrecognized viruses

• Universal precautions and other legal requirements, as outlined by the Centers for Disease Control, which must be observed

• Documented sources of cells or tissues; certificate of test results should be available if commercial sources used

• Performing work in a biological safety cabinet (vertical laminar flow hood) to protect the operator and preserve the sterility of the test system

• Regular disinfection of surfaces to reduce contamination

• Sterilization of spent medium, plasticware, and cell cultures before disposal

9.5.2 *In vivo* Methods

In vivo methods refer to experiments done in the living whole animal. Mostly exposure studies are conducted after the intentional or non-intentional exposure to the chemicals solid and liquid biopsies will be taken and analyzed. In extreme toxicology assays, sometimes laboratory animals are exposed and sacrificed in order to perform in-detail analyses as well. A biopsy is basically a test involving the extraction of cells or tissues from a living organism for analysis for determination of potential diseases or abnormalities.

9.5.2.1 Acute and Chronic Toxicity Assessments

Acute toxicity is defined as the effects that occur upon being exposed to a toxin for a short period of time usually in high doses. The most common measure is the lethal dose (LD_{50} value). This is defined as the dose required to kill *half the members of a specific animal population* when entering the animal's body by a particular route, which may be oral, dermal or vapour. It is calculated by introducing different levels of doses to target populations mainly laboratory animals like rats, then observing the number killed in order to measure it. The value is then correlated to humans, which is used for decision making in legislation on chemical usage including PBTs.

Chronic toxicity is the development of adverse effects in relation to exposure to toxins for a longer period of time in low doses. Aquatic organism populations are exposed for an extended period of time and the results are observed. Common organisms used in this study include, Fathead minnow fish, *Pimephales promelas*, larval survival and growth and Daphnia, *Daphnia magna*, 21-d survival and reproduction

Another very important value is the NOEC which stands for **No Observed Effect Concentration**. It is the concentration of a toxin that will have no effect on the species

concerned. Populations of the same species are treated to different concentrations and the target parameter is observed. Similarly, the no-observed-adverse-effect level (NOAEL) denotes the level of exposure of an organism, found by experiment or observation, at which there is no biologically or statistically significant increase in the frequency or severity of any adverse effects of the tested protocol.

The EC_{50} which stands for **Half maximal effective concentration** is the concentration of chemical in water to which test organisms are exposed that is estimated to be effective in producing some sublethal response in 50% of the test organisms. The EC_{50} is usually expressed as a time-dependent value (e.g., 24-h or 96-h EC_{50}) (Derelanko and Hollinger 2002).

9.5.2.2 Animal Generation Studies (Prenatal Exposure Effects)

These are studies, which involve the toxic adverse effects, which may be inherited to the next generation. For example, Arfsten et al 2009 implanted Depleted Uranium (DU) pellets in adult rats and had the generation be subjected to mating. The offspring were obtained and compared with control experiment rats, which were implanted with inert Tantalum pellets. The offspring were found to have a higher death rate post weaning and higher mean heart weights. Sometimes these studies are called as transgenerational studies.

9.5.2.3 Safety Precautions in in vivo Testing

If *in vivo* animal models are used for toxicity assays, there are mandatory accepted biosafety and animal ethical procedures

- The handlers/researchers must be specially trained for the purpose. Usually, a license is required to perform animal studies.
- Facilities must be fit and suitable for the purpose of the work; that is, size, construction, and location should be appropriate, and the building should allow for the separation of activities.
- Air handling systems should be operated to ensure that the correct environment is maintained for the type of work conducted in the laboratory
- Animals must be sacrificed in a humane way using accepted laboratory animal research protocols
- Disposal of spent tissues and organs etc. must be done properly

9.5.2.4 Animal Testing Protocols.

The use of animals in toxicological experiments is strictly controlled by regulations and protocols. Different countries and regions have different protocols, but most of them have following in common

1. a justification for using animals, the number of animals to be used, and the species chosen,
2. the procedures or drugs to be used to eliminate or minimize pain and discomfort,
3. a description of the methods and sources used to search for alternatives to painful procedures, and
4. a description of the search used to ensure that the experiment does not unnecessarily duplicate previous research.

In Sri Lanka, the use of animals in experimental work is regulated under the Animal Welfare Bill- 2006 and the permits for conducting experiments involving animal should be obtained from the Animal Welfare Authority.

9.6 Exposure biomarkers

The National Institutes of Health Biomarkers Definitions Working Group defined a biomarker as "a characteristic that is objectively measured and evaluated as **an indicator** of normal biological processes, pathogenic processes, or pharmacologic responses to a therapeutic intervention" (Biomarkers Definitions Working Group, 2001). There are 3 types of biomarkers namely;

1. Biomarkers of susceptibility
2. Biomarkers of exposure
3. Biomarkers of effect

Biomarkers of exposure are very important in determining whether an individual has been exposed to several health threatening PBTs. Both *in vitro* and *in vivo* toxicity assays use biomarkers to measure the exposure response if they are known and new researches are being conducted every day to find novel biomarkers to predict the exposure to different chemicals including PBTs. For example, Nordberg et al 2005 investigated several 619 people living in metal contaminated areas in China and discovered elevated levels of proteins in urine such as urinary beta(2)-microglobulin (UB2MG), N-acetyl-beta-glucosaminidase (UNAG), retinol binding protein (URBP) and albumin (UALB). In addition, high levels of Cadmium and Arsenic were found in urine compared to uncontaminated areas. As discussed earlier, chemicals play a large role in coordinating metabolic activities in the body with heavy metals acting as enzyme

inhibitors. In the above example, it disrupted normal metabolic reactions causing a spike in the above proteins. In addition to observing symptoms, analysis of the relevant biomarkers may also provide insight to identification of mass exposure in order to prevent the adverse impacts of PBTs.

The difference between Biomarkers and Symptoms

Symptoms are signs of ill health or disease as perceived by the patient or observer. Biomarkers do not necessarily fall into this category as they can be measured accurately and reproducibly. For example, fever is a symptom and elevated levels of antibodies is a biomarker.

9.7 'One Health' Concept

'One Health' is an approach to designing and implementing programs, policies, legislation and research in which multiple sectors communicate and work together to achieve better public health outcomes. The 'One Health' approach is critical to addressing health threats in the animal, human and environment interface.

The areas of work in which a One Health approach is particularly relevant include:

- food safety
- control of zoonotic diseases
- laboratory services
- neglected tropical diseases
- environmental health
- antimicrobial resistance

The 'One Health' approach is of importance in specifically mitigating the contamination due to PBTS and unwanted exposure to PBTs as well.

9.8 Conclusion

PBTs (Persistent, Bioaccumulative and Toxic Chemicals) are an extremely high risk in the world at present due to its highly developing nature. They cause a variety of adverse health effects due to disrupting the body's normal cellular, metabolic and coordination activities resulting in diseases such as the Minamata disease in Japan. Therefore, in order to negate their effects, a thorough understanding must be present about their ill effects on different organ systems for legislation to be passed in banning their production and use.

Analysis of the toxicological effects of PBTs must be extremely accurate, since most PBTs are widely used commercially, for different commercial purposes on which people's livelihoods are dependent. On the other hand, their exposure to humans, animals and the environment causes major disruptions in ecological cycles. It is evident that though we have identified more than 4000 toxic chemicals at present, monitoring and action is only managed on a small number on this list. Therefore, a correct use of toxicology with regard to PBTs provides critical information and knowledge that can be used by regulatory agencies, decision makers, and others to put programs and policies in place to limit our exposures to these substances, thereby preventing or reducing the likelihood that a disease or other negative health outcome would occur.

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