DECHLORANE PLUS: CANDIDATE POP IN STOCKHOLM CONVENTION

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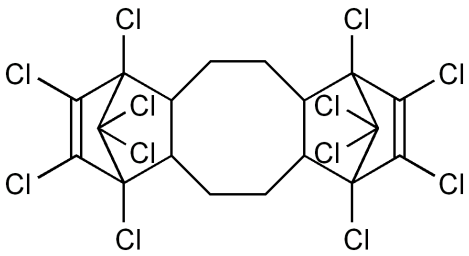
INTRODUCTION

Dechlorane Plus or Bis(hexachlorocyclopentadieno) cyclooctane, ($C_{18}H_{12}Cl_{12}$, DP) is a polychlorinated flame retardant designed in the late 1960s to substitute Mirex (also known as Dechlorane)[1].



Chemical structure of Dechlorane Plus

The chemical structure of DP and its physical-chemical properties are similar to those of internationally banned organochlorine pesticides, such as aldrin, dieldrin, chlordane, heptachlor and mirex, which were among the initial "dirty dozen" enlisted in the Stockholm Convention[2].

With the global restriction of brominated flame retardants (FRs) such as deca-BDE, octa-BDE, the use of other FRs like DP has increased[3]. It is preferably used owing to its low cost, low density, and high thermal and photochemical stabilities than the other brominated flame retardants[4].

The commercially available formulation of DP contains two stereoisomers, syn-DP and anti-DP in the approximate ratio of 1:3. Three types of DP products are available commercially (DP-25, DP-35, and DP-515). All of them have same chemical composition but differ in particle sizes.

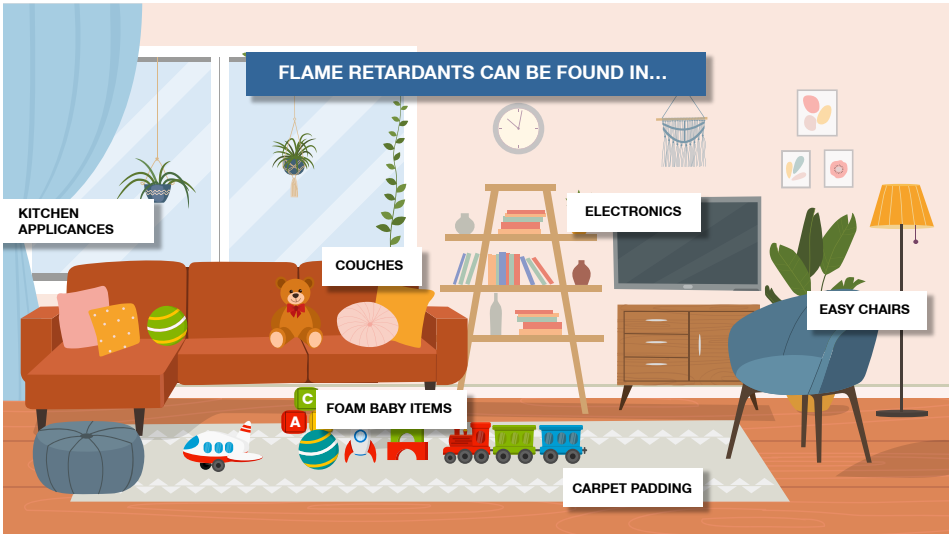
DP does not occur naturally and is released to environment most likely through manufacturing, formulation and/or industrial usages. It has been detected in groundwater and lakes at certain sites.

CHARACETRISTICS

- Solid white powder
- Highly chlorinated
- Poorly soluble in water
- Extremely lipophilic
- Photostable
- Persistent in the environment, subject to long-range atmospheric transport, bio-magnification and bioaccumulation in biota through the food chain
- Half-life in water is >24yrs, in sediments app 17yrs
- Log K_{ow} = 9.3

USAGES

The Dechlorane Plus technical mixture is a commercially available polychlorinated FR. It is used as an additive FRs in electrical wire and cable coatings, plastic roofing materials, wallpapers, connectors in TV and computer monitors, and as a non-plasticizing FR in polymeric systems, such



as nylon, Styrene butadiene rubber (SBR) block copolymer, polyester resins and polypropylene plastic.

As per the REACH registration dossier, in the EU, DP is not used as an intermediate during industrial manufacturing processes.[5] While US EPA suggests that DP is also used as an intermediate in production processes in various industries such as in chemical manufacturing, production of metals, the cosmetics industry, and for production of a variety of products (US EPA, 2002).

According to ECHA (2019c), the concentration of DP in finished articles is typically around 20%.[6]

PRODUCTION

DP has been manufactured since the 1960s, and production has been reported from Europe (The Netherlands and Sweden), the United States, and China. It is registered as a high-production volume chemical in the United States with the annual global production estimated at~5 kt.[7] Currently, there are two known producers of Dechlorane Plus in the world: one located in the North America and the other in China.[8]

Summary of uses of DP found in open literature as identified in ECHA (2022b)

Industry	Sector	Article / Component
Automotive	Electrical and electronic equipment	Wires and cable plastic coatings, coil bobbins, cable straps
		Switches, and small electronic appliances including cameras, computers (motherboards, chargers and hard-plastic connectors)
	Engines	2-part epoxy-void fillers
	Other	Bodywork parts
Aviation	Electrical and electronic equipment	Wires and cable plastic coatings, coil bobbins, cable straps
		Switches, and small electronic appliances including cameras, computers (motherboards, chargers and hard-plastic connectors)
	Engines	2-part epoxy-void fillers
Electrical / electronic equipment	Wires and cables	Wire and cable plastic coatings not used in the automotive or aviation industry, including cable insulation and nuclear power plant control cables
	Electronic devices	Electronic devices not used in the automotive or aviation industry, including mobile phones, lamps, refrigerators, computer and washing machines
Building /manufacturing materials	Plastic products	Plastic roofing materials, wallpaper, paint, pipes, flooring, power tool housing and wall plates
Other consumer products	Plastic products	(Plastic) toys
		Food packaging
	Textiles	Clothing, mattresses, curtains, carpets and (textile) toys
	Adhesives	Adhesives and binding agents, syntactic foams and potting compounds

Global volumes of DP per use application

Uses		Share of total	Low-volume scenario (t/y)	High-volume scenario (t/y)
Polymers	board housing, other plastic and rubber parts	93%	279	930
Adhesives etc.	Tape, adhesives, sealants	5%	15	50
Greases	Lubricant	2%	6	20
All		100%	300	1,000

Global volumes of DP per sector according to the stakeholder consultations

Sectors	Low volume scenario		High volume scenario	
	Share of total	Use volume (t/y)	Share of total	Use volume (t/y)
Automotive	75%	225	57%	565
Aviation	10%	30	10%	100
Other	15%	45	33%	335
All	100%	300	100%	1,000

EXPOSURE ROUTE

The potential routes of exposure includes inhalation and dermal contact during manufacturing, processing or use of DP.[9] DP have been detected in environmental samples and humans living near e-waste recycling sites and production plants. DP is also detected in dust, sludge and wastewater from WWTPs indicating emission and exposure from consumer products throughout their lifecycle. Monitoring data indicate that the general population may be exposed to DP from indoor dust, food, ambient air, water, soil, sediment and breast milk and some foods such as fish and sea-foods.[10], [11]

The bioaccumulation trend of DP in various tissues is kidney > liver > muscle tissues. Additionally, gender-based accumulation trends revealed high DP levels in females in comparison to males due to strong metabolism of males.[14]

Adverse health impacts of Dechlorane plus:

- Pancreatic dysfunction
- Adipose tissue dysfunction
- Liver impairment
- Predisposition to type II diabetes
- Endocrine effects
- Oxidative stress
- Disruption of thyroid hormone receptor signaling
- Attention deficient hyperactivity disorder (ADHD)
- Potential for neurotoxicity and/or hepatotoxicity

HEALTH IMPACTS

DP has been detected in human blood and breast milk from several countries. POPRC-17 has submitted the detection of DP worldwide in human tissue, including placenta, cord blood, breast milk, adipose tissue, and hair, with high exposures in toddlers and young children, as well as high occupational exposures. DP is linked to ageing and to diseases in animals, and has potential for endocrine disruption and liver impairment in humans[12].

Estimated daily intake (EDI) via dust ingestion for toddlers and adults reported were 0.20 and 0.02 ng/kg bw/day[13]

ENVIRONMENTAL IMPACTS

A number of activities such as production, use, recycling and waste handling, as well as landfill leachate and run-off and wastewater treatment, can lead to releases of DP to the environment. Occurrence of DP in both biotic and abiotic environmental matrices has been confirmed by various research studies[15]. Large-scale distribution of Dechlorane plus had been reported in air and seawater from the Arctic to Antarctica.[16]

Due to the extensive use in the electrical appliances DP has been reported in both indoor as well as outdoor dust in several countries. Similarly, DP has been reported in fish, egg, meat and poultry,

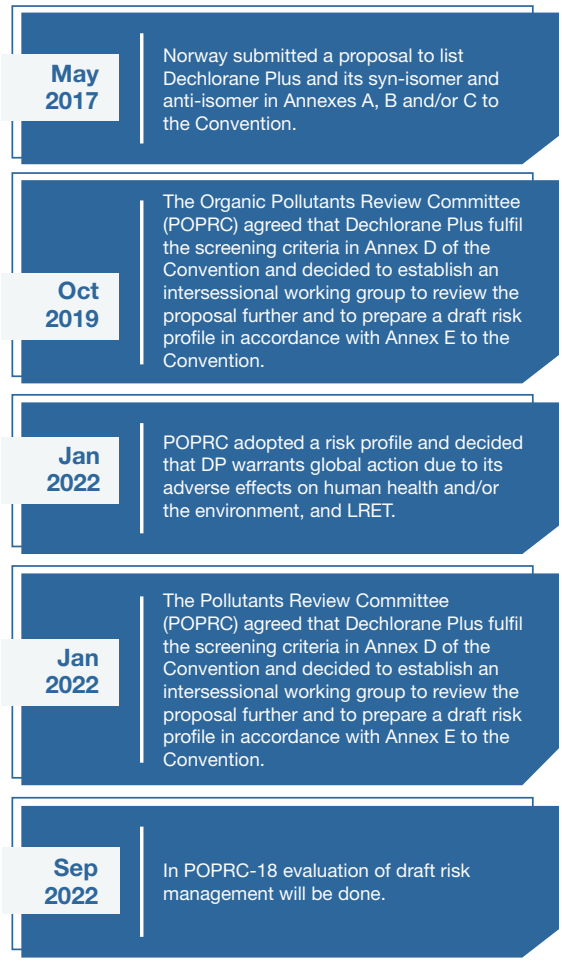
milk and dairy products, sugar and confectionary, legumes and fats and oil samples.[17]

No acute toxicity has been observed for DP in birds, but studies indicate that DP is bioavailable and transferred to eggs.

REGULATIONS

Stockholm Convention

Considering the characteristics of persistence, bio-magnification and bioaccumulation Dechlorane plus is under consideration in the Stockholm Convention.



Global Scenario

DP is currently not known to be included in any international Conventions; however, regulatory processes has been initiated in several countries.

- Enlisted on Canada's Domestic Substances List (DSL) under which products can only be import in quantities of 0.1 ton not more (ECCC, 2019)[18].
- In 2018, DP was identified as Substances of Very High Concern (SVHC) and added to the REACH Candidate List due to their persistent and bio-accumulative properties[19].
- In the United States, DP is listed under the Toxic Substances Control Act (TSCA) inventory and is subject to the Chemical Data Reporting Rule.
- In Norway, DP was enlisted as priority substances in January 2019 with a national goal to phase out the use by 2020[20].
- In Egypt DP is banned by Decree No. 55 year 1996 of the Minister of Trade.
- DP has been listed on the International Chemical Secretariat's (ChemSec) Substitute It Now (SIN) List since 2014 (SIN LIST) based on the criteria defined within REACH, the EU chemicals legislation.

STATUS IN INDIA

There is no information available on the export, import and usages of DP in India.

However, DP has been reported in air samples collected from 15 homes in Patna in the range of 0.2 to 5.43 pg/m^3 (median 2.81 pg/m^3) and 0.52–62.7 pg/m^3 (median 1.62 pg/m^3) for urban and suburban sites, respectively (Yadav et al., 2020). Another study has reported the median concentration of syn-DP as 63% and 65% of indoor and outdoor dust respectively[21].

In 2020 the Society of Indian Automobile Manufacturers (SIAM) submitted to the POPRC that DP is used as an alternative to c-decaBDE in automobile manufacturing.[22] While, in POPRC-17, Jan 2022, India has suggested for more information about the socio-economic implications of global action on Dechlorane Plus, especially on developing countries and countries with economies in transition, before making a decision.

ALTERNATIVES

Several chemicals are in use and reported as an alternative to existing brominated flame retardants by Stockholm Convention and EU REACH. Chemical substitutes currently used comprise the group of [xv]:

a. *Organophosphorus compounds:*

- Halogenated: tris-chloropropyl-phosphate (TCPP), tris-chloroethyl-phosphate, and tris dichloropropyl phosphate (TDCPP),
- Non-halogenated: triphenyl phosphate (TPP), tricresyl phosphate (TCP), resorcinol bis(diphenylphosphate) (RDP), and phosphonic acid (2-((hydroxymethyl) carbamyl)ethyl)- dimethyl ester

b. *Inorganic fire retardants:* mainly used for coatings and lacquers e.g., aluminium trihydroxide, magnesium hydroxide, red phosphorus, zinc borate etc.

c. *Nitrogen containing compounds:* Ammonium polyphosphate in combination with aluminium hydroxide and melamine is used as flame retardants for polyurethane foams. Other compounds are melamine cyanurate and melamine polyphosphate.

It must be noted that several of these alternatives especially organophosphorus compounds like TCPP, TPP, RDP are also hazardous in nature and their potential impact on human health & the environment are under scrutiny. Nitrogen containing products with melamine have been reported hazardous due to the PBT/ED properties. THESE CHEMICALS ARE ON THE CoRAP-LIST IN ECHA.

There are some generally safe chemicals with low concern has been identified such as Aluminium diethylphosphinate (Alpi), Aluminium hydroxide (ATH), Ammonium polyphosphate (APP), Melamine polyphosphate (MPP), Dihydrooxaphosphaphenanthrene (DOPO), Zinc stannate (ZS), Zinc hydroxstannate (ZHS)[23].

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