CHLORINATED PARAFFINS

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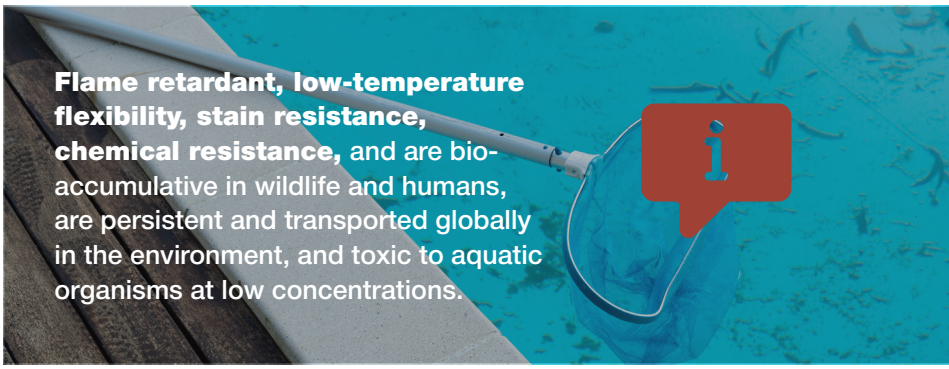
INTRODUCTION

Chlorinated paraffins (CPs) are mixtures of polychlorinated n-alkanes formed through the chlorination of paraffins fractions under conditions of high temperature and/or ultraviolet irradiation. These complex CP mixtures contain congeners that differ based on carbon chain length, chlorination level, chlorine position on the chain, and carbon atom stereochemistry. There are predicted to be over 10,000 possible isomers. [1, 2] (**Figure 1**)



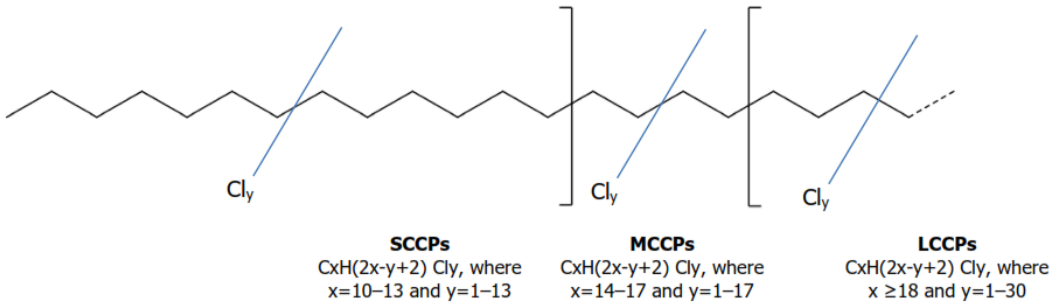


Figure 1: General structure of chlorinated paraffins (CPs)

CPs have been produced commercially since the 1930s. These mixtures of chlorinated *n*-alkanes are produced by reacting normal paraffin fractions obtained from petroleum distillation with gaseous chlorine exothermically at 80–120°C in the liquid phase.[3]

Meanwhile, technical CP mixtures are commonly produced, labelled, and traded according to their chlorine content. Thus, different chain lengths are often present in technical CP mixtures at varying proportions, according to the product and the manufacturer[4, 5]

The chemical can also be categorized into high-chlorinated CPs and low-chlorinated CPs based on the chlorine content. This type of categorization is often used in Asian countries: for example, the commercial CP products in China are named CP-42, CP-52, and CP-70 according to the chlorine content by weight. The weight content of chlorine generally ranges between 30 and 70 %.[6]

Types of CP or its categorization

CPs are generally divided into three groups based on their carbon chain lengths:

- Short-chain chlorinated paraffins (SCCPs, C10–13 and a chlorine content of 40-70%).
- Medium-chain chlorinated paraffins (MCCPs, C14–17 and a chlorine content of 40-70%).
- Long-chain chlorinated paraffins (LCCPs, C≥18).

India and China are the major contributors to its global production. The current global production of CPs is around **2 million tons** with China leading the production of **1.05 million tons** of CPs, whereas India accounts for the second largest production of CP.

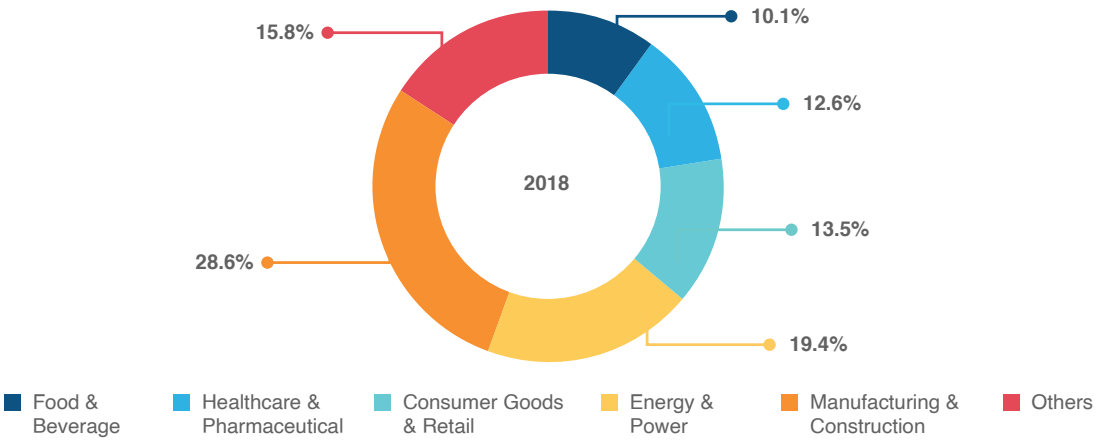


Figure 2: Sector specific application of CPs
(Source: https://www.openpr.com/news/1796712/chlorinated-paraffin-market-outlook-to-2027-quimica-del-cinca)

Production and usage

According to the market survey report, the CP market was valued at USD 1.92 Billion in the year 2022 and is expected to reach at USD 2.80 Billion by 2029, with a CAGR of 5.45%.[7] (**Figure 2**).

Currently, the global production of CPs has been estimated to be approximately 2 million metric tonnes (t) Based upon the facts it has been observed that CP is produced by several countries, but India and China are the major contributors to its global production[8]. The current global production of CPs is around 2 million tons with China leading the production of 1.05 million tons of CPs[9], whereas India accounts for the second largest production of CP.[10, 11] **(Figure 3)**

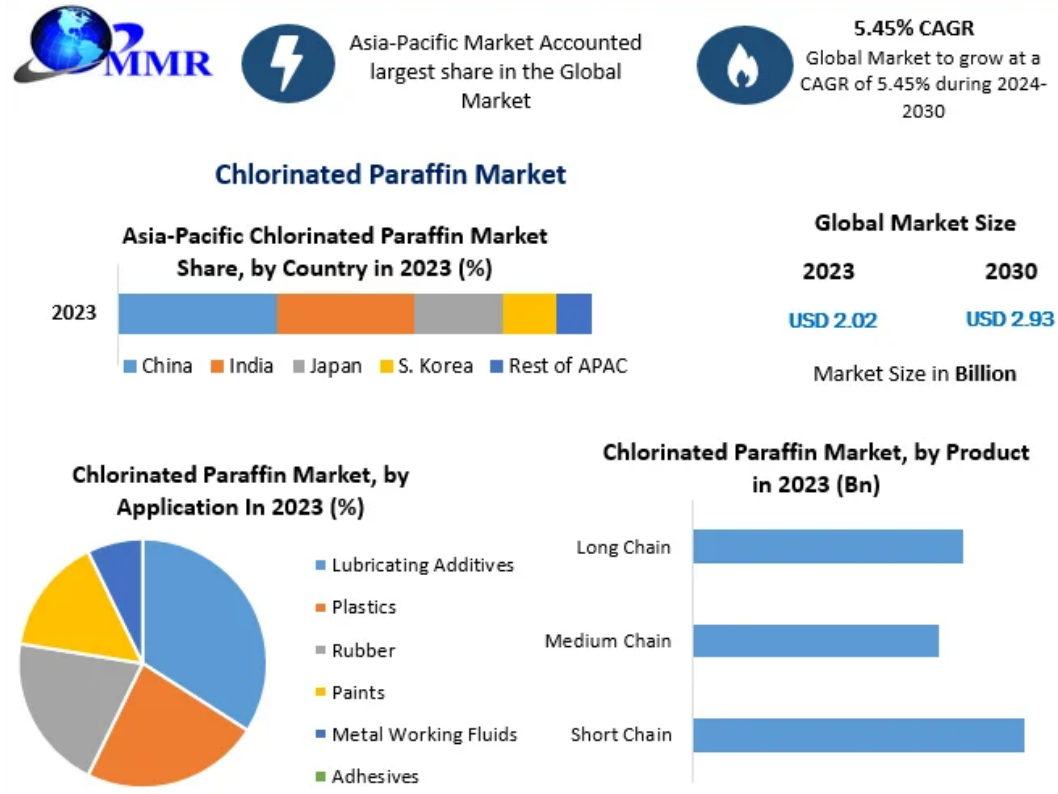


Figure 3: Market overview of CP
(Source: https://www.maximizemarketresearch.com/market-report/chlorinated-paraffin-market/168799/)

According to Chen et.al., (2021)[12], as of 2019, China sees an estimated 650000 tonnes of SCCPs and MCCPs production annually. It has also been reported that 88% of the annual production of SCCPs, accounting to 235,000 tons, and 74% of MCCPs, totaling 415,000 tons, have been utilized in polyvinyl chloride (PVC) production, followed by rubber which constitutes SCCPs up to 5% and MCCPs up to 18%. The polyurethane foam adhesives, utilizing 5% SCCPs and 6% MCCPs. Whereas, in metalworking fluids and leather production, only 2% of SCCPs and MCCPs are used. This dominance of CP application within polymer products appears consistent across various regions.

Status of chlorinated paraffins in India:

India imports and exports Chlorinated Paraffins (CP) using two distinct HS Codes:

- HS Code 27129090: Paraffin waxes
- HS Code 38122090: Plasticizer compound (https://www.dgft.gov.in/CP/),
- India imports Chlorinated Paraffins in the form of paraffin waxes, while exports predominantly involve plasticizer compounds (**Figure 4** and **Figure 5**).
- In 2022-2023, India imported paraffin waxes (CP) primarily from UAE, China, Thailand, Germany, Spain, Malaysia, and Korea. Conversely, plasticizer compounds (CP) were predominantly imported from Japan, China, Korea, Germany, the Netherlands, and the USA (**Table 1 and Table 2**).
- India predominantly exports plasticizer compounds to countries like Nepal, Malaysia, Poland, Indonesia and Bangladesh.
- Specific data regarding individual CP mixture categories (SCCPs, MCCPs, LCCPs) and sector-wise consumption within India is currently unavailable.

88% of the annual production of SCCPs, accounting to 235,000 tons, and **74%** of MCCPs, totaling 415,000 tons, have been utilized in polyvinyl chloride (PVC) production, followed by rubber which constitutes SCCPs up to **5%** and MCCPs up to **18%.**

Table1: Import data of CP in the country (2022-2023)

Country	Import data of CP	
	Paraffin wax	Plasticizer compound
	Quantity (Thousand tonnes)	
UAE	19568.3	--
China	8832.13	6190.37
Thailand	2344.67	--
Germany	1233.62	220.67
Spain	1639.28	--
Korea	1175.99	389.03

Table 2: Export data of CP in the country (2022-2023)

Country	Export data	
	Paraffin wax	Plasticizer compound
	Quantity (Thousand tonnes)	
Australia	131.98	--
UAE	96.24	--
Nepal	73.53	2569.82
Malaysia	48.06	1539.78
Germany	24.29	--
USA	19.39	--
Poland	0	1715.88
Indonesia	0	1588
Bangladesh	0	2281.57

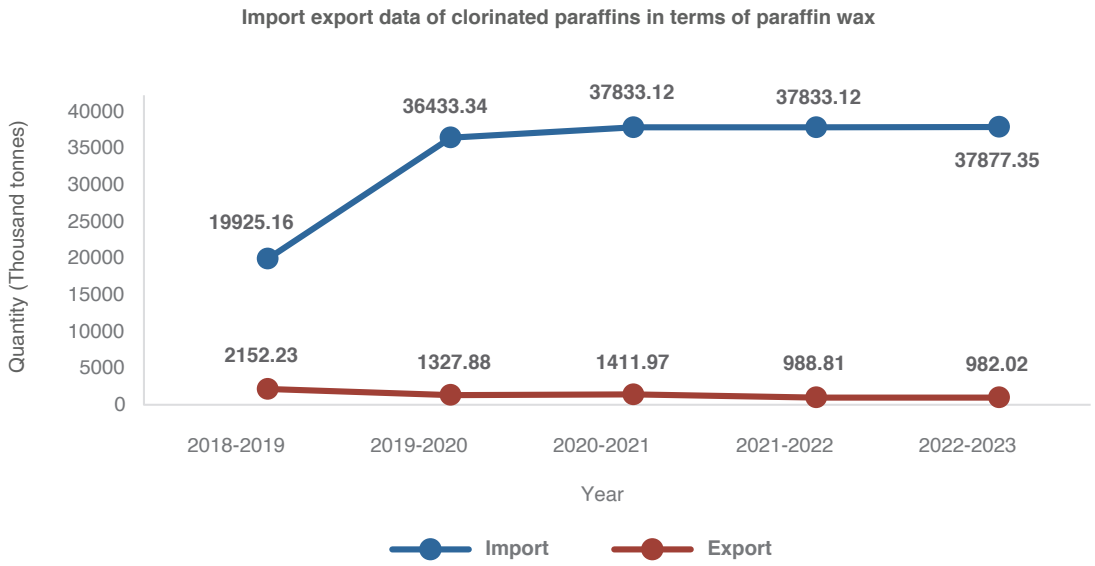


Figure 4: Import export data of clorinated paraffins (Paraffin wax)

CP also improves water resistance, which is an essential additive to marine paints, coatings for industrial flooring, vessels, and swimming pools.

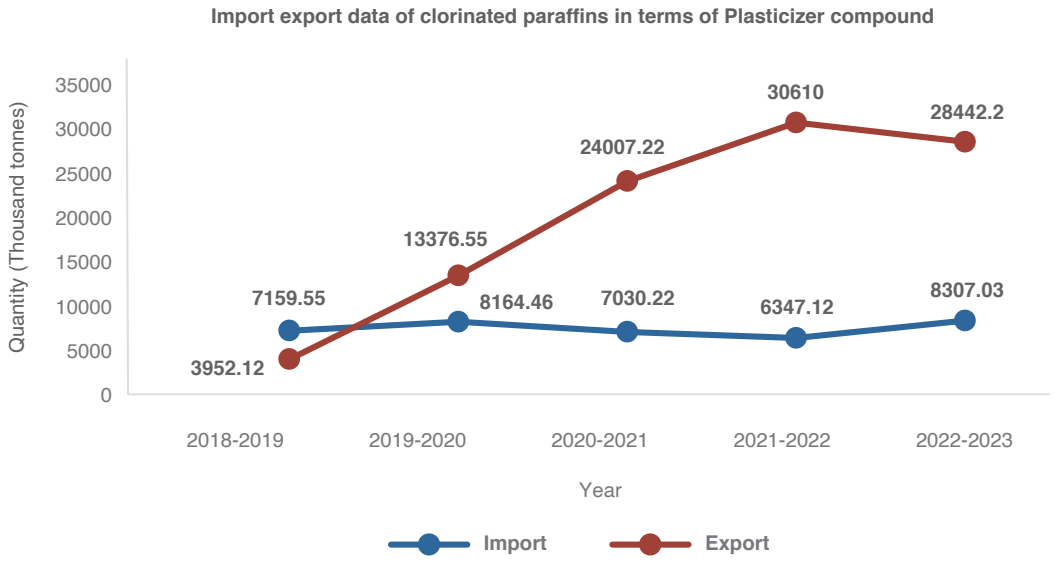


Figure 5: Import export data of chlorinated paraffins (Plasticizer compounds)

SHORT-CHAIN CHLORINATED PARAFFINS (SCCPs):

Applications

SCCPs are a complex chemical which has a wider industrial application such as plasticizers, flame retardants, lubricant additives, improving adhesion, adhesives, and sealants, while also finding utility in rubber compounding and leather processing. It is often used as a coolant or lubricant in metal cutting or forming.

In addition, CP also improves water resistance, which is an essential additive to marine paints, coatings for industrial flooring, vessels, and swimming pools. **(Figure 6)**

The exposure of SCCPs to human health can be correlated with their presence in food stuff, plants, wildlife, human tissues and various environmental matrices.

Figure 6: Application of CPs in coating for swimming pools

- It is mainly used as a flame retardant in conveyor belts, V belts, and natural & synthetic rubber.
- It is used as a plasticizer in the formulation of PVC compounds & granules used in wires & cables, PVC windows and door profiles, PVC flooring, films & sheets, PVC footwear, etc.
- Used in Polyurethane and polysulfide-based sealants and adhesives.
- As an extreme pressure additive in metal working fluids / cutting compounds.
- As a flame retardant in the paint industry in the formulation of swimming pool paints and other fireproof paints.
- As a flame retardant in the textile industry in finishing of heavy textiles such as military tents.

Routes of Human Exposure

The unintentional sources of SCCPs in the environment may be due to their production, storage, leaching and runoff.

Many research studies have reported human exposure to SCCPs through unintentional ingestion via indoor dust inhalation and dietary intake[13,14,15]. Studies also showed the occurrence of SCCPs in human samples[16, 17] food[18] and wildlife[19].

The exposure of SCCPs to human health can be correlated with their presence in food stuff, plants, wildlife, human tissues and various environmental matrices.[20] **(Figure7)**

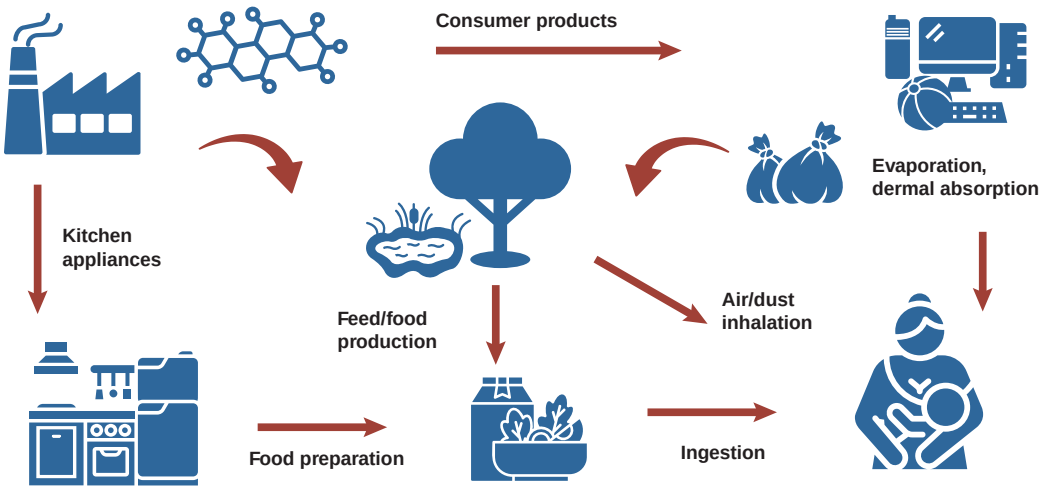


Figure 7: Route of Human Exposure of SCCPs

Health Impacts on Exposure

Emissions from SCCPs may be harmful to ecosystems and people's health, considering their widespread use and massive output quantities[21, 22].

According to the research studies, SCCPs may pose liver and kidney toxicity, reproductive toxicity, an endocrine disorder, neurotoxicity, immune dysfunction, and developmental toxicity[23].

SCCPs have been reported in blood, breast milk, and umbilical cord blood.[24, 25, 26, 27]

Environmental reports have indicated that SCCPs are toxic, persistent, bio-accumulative, and dispersive compounds, with the exception of their specificities[28]. **(Figure 8)**

The Basel Convention has suggested two preliminary limits for low levels of SCCPs in wastes. These limits are set at **100 mg kg^{-1}** and **10,000 mg kg^{-1}**

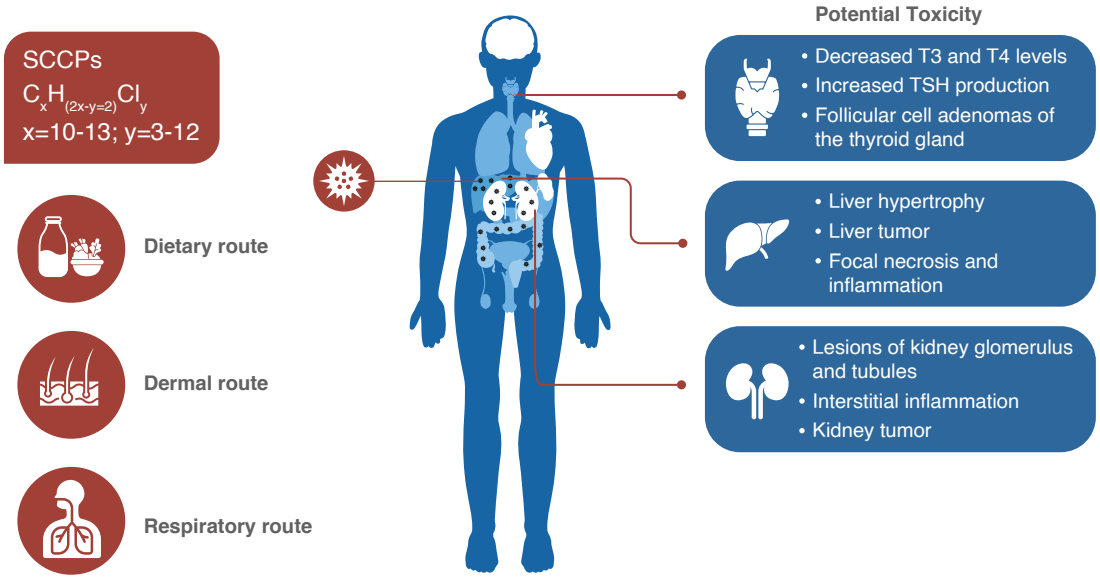


Figure 8: Human Health Impacts of SCCPs Exposure

Status in Stockholm Convention

In May 2017, SCCPs were included in Annex A of the Stockholm Convention. However, certain exemptions were granted for specific applications for mining and forest industries, leather production, lubricant additives and plasticizer of PVC except for toys and children's products.[29, 30, 31].

The Basel Convention has suggested two preliminary limits for low levels of SCCPs in wastes. These limits are set at 100 mg kg^{-1} and 10,000 mg kg^{-1}. Products exceeding these limits should be destroyed or transformed in an environmentally safe manner[32,33].

International Regulatory Actions Vs Indian Scenario

Efforts are underway to align India's regulatory standards with international conventions such as the Stockholm Convention on Persistent Organic Pollutants, signalling a commitment to address SCCPs comprehensively. However, the specific measures and timelines for implementation are still being formulated, reflecting the complexity of transitioning away from SCCPs while ensuring the continuity of industrial processes reliant on these chemicals. **Table 3** represents the status of the regulatory framework of SCCPs.

(MCCPs) are a mixture of chlorinated hydrocarbons with a chain length of **14 to 17** carbon atoms, and the same chlorine content range of **40-70%.**

Table 3: Regulatory framework of SCCPs (Global vs India)

Year	Country	Regulation	Remark
2024	Australia	Industrial Chemicals Environmental Management Standard	Australia is Prohibiting SCCPs from July 2024 in Industrial Chemicals Environmental Management Standard (IChEMS) Register Schedule 7
2023	China	Chinese Ministry of Ecology and Environment (MEE)	Restricted the use of SCCPs from 1st Jan 2024.[34]
2023	Vietnam	National Technical Regulation on Thresholds for Persistent Organic Pollutants (POPs)	Vietnam proposes a draft version to restrict SCCPs in certain items. (1% in substances or mixtures)[35]
2018	Singapore	National Environment Agency (NEA)	The National Environment Agency (NEA) off Singapore notified the WTO TBT Committee showed its intentions towards phasing out of SCCP for production, import/export and application.
2012	European Union (EU)	EU Regulation No 519/2012	Included SCCP in Annex I of Stockholm convention on POPs. However specific exemptions for production and market use up to 1% were granted for certain uses of SCCPs.
India	Currently, India doesn't have any specific policy for chlorinated paraffins		

Alternatives

- Non-chlorinated paraffins such as alkylphosphates and Sulfonated fatty-acid esters can be used in specific applications
- Leather production: Natural animal and vegetable oils.
- Paint and coating: Polyacrylic esters, diisobutyrate and phosphates.
- Flame retardant: Aluminum hydroxide and phosphate-containing compound.[36]
- Metalworking fluid: Alkanol amides, Isopropyl oleate, Long-chain chlorinated paraffins (C18+) (LCCPs), Medium-chain chlorinated paraffins (C14-17) (MCCPs), Nitrated compounds and Overbased calcium sulphonates
- Phosphorus-based compounds: alkyl phosphate esters, Phenol, isopropylated, phosphate, Tributyl phosphate, Triaryl phosphate, bis(2-ethylhexyl) hydrogen phosphate, didodecyl phosphite, Dimethyl hydrogen phosphite, 2-ethylhexyl hydrogen phosphate, Polyethoxy oleyletherphosphate, Zinc dialkyldithiophosphates and Zinc Dialkyl Dithiophosphate.
- Sulphur-based substitutes: Sulphurized polyisobutene, polypropylene, polystyrene, Tertiary nonyl polysulfide, Polyolefin sulphide, Sulfonated fatty acid esters, Polysulphides, alkyl sulphide, sulphurized alkenes/olefins, and sulphurized hydrocarbons[37]

MEDIUM-CHAIN CHLORINATED PARAFFINS (MCCPs)

Medium-Chain Chlorinated Paraffins (MCCPs) are a mixture of chlorinated hydrocarbons with a chain length of 14 to 17 carbon atoms, and the same chlorine content range of 40-70%.

Application:

- As flame retardants in plastics, PVC cables, flooring materials, automobile, rubbers, textiles and paints.
- As additives and lubricants in metalworking fluids reducing friction and wear during machining operations such as cutting, drilling, and grinding.
- As plasticizers in PVC formulations, helping to improve the flexibility and durability of the polymer.
- MCCPs are incorporated into adhesives and sealants to improve their performance characteristics. They act as viscosity modifiers, enhancing the workability and adhesive properties of the formulations.
- MCCPs are used in leather processing as fat liquors, which help in softening and lubricating the leather fibres.

Routes of Human Exposure

- Unintentional ingestion of MCCPs through food[38], water[39], soil[40] and wildlife[41].
- Exposure of MCCPs by inhalation from air stacks emission.
- Dermal exposure through handling of products containing MCCPs.
- MCCPs can enter the environment through various pathways, such as release during manufacturing, use, and disposal. **(Figure 9)**

Faecal excretion is the primary elimination route, with urine and exhaled air contributing less than **3%** and **0.3%** to excretion, respectively.

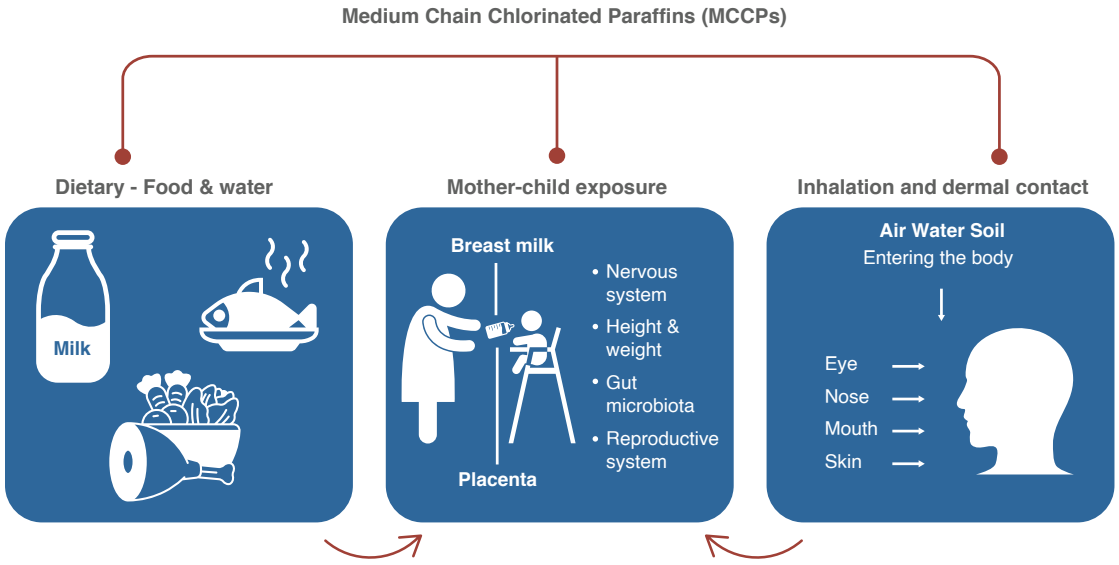


Figure 9: Sources of MCCPs exposure to humans

Health Impacts on Exposure

- Inhalation studies for MCCPs are unavailable, but it's assumed that inhalation absorption won't exceed 50%.[42]
- Oral absorption of MCCPs is significant, likely absorbing at least 50% of the total dose.
- Dermal absorption studies are lacking, yet an in-vitro study suggests around 1% absorption rate[43].
- MCCPs are found in various tissues post-absorption, including liver, kidney, ovaries, adrenal glands, and adipose tissue[44]. Initial concentrations are highest in liver and kidney, but they decrease within days.
- Accumulation in adipose tissue occurs, with elimination half-lives ranging from 2 to 8 weeks.
- Metabolism involves conjugation with glutathione and CO_2 production, with a reverse correlation to chlorination degree.

- Faecal excretion is the primary elimination route, with urine and exhaled air contributing less than 3% and 0.3% to excretion, respectively. Based on previous scientific studies, MCCPs have been detected in human blood in China[45, 46, 47, 48, 49]
- Various research has reported the concentration of MCCPs in Chinese blood in the range of 470 ng/g lw to 15,200 ng/g lw respectively.[50, 51, 52] Whereas the concentration of MCCPs in the Australian population's blood was found to be 190 ng/g lw, respectively.[53]

Status in Stockholm Convention

In its ninth meeting held on October 2023, POP RC-19 committee of the Stockholm Convention has recommended for listing of MCCPs in Annex A, with several specific exemptions, such as for metalworking fluids, PVC, adhesives, sealants, and tape used for non-structural bonding in aerospace and defence products. The decision will be finalized hopefully in the upcoming POPRC-20 session[54]

Global Regulations on MCCPs

Several countries are imposing restrictions or regulations on MCCPs due to their Persistent, Bio-accumulative, and Toxic (PBT) properties. **Table 4** illustrates the regulatory status of MCCPs worldwide.

Various research has reported the concentration of MCCPs in Chinese blood in the range of **470 ng/g lw** to **15,200 ng/g lw** respectively.

Table 4: Regulatory status of MCCPs

Year	Country	Regulation	Remark
2024	Singapore	Environment Protection Management Act (EPMA) and Environment Protection and Management (Hazardous Substances)	Singapore notifies proposal to regulate the MCCPs in products. The regulatory measures will be promulgated in the official gazette by June 2024.[55]
2023	China	Ministry of Ecology and Environment of China	The Ministry of Ecology and Environment of China issues a notice for collecting information on production, usage, import export, alternative substances and alternative technologies of MCCPs for POP RC-19 of the Stockholm convention.[56]
2022	European Union	ECHA	ECHA updated the information for their intentions for restricting medium-chain chlorinated paraffins ECHA will update the intention to submit an Annex XV restriction dossier on medium-chain chlorinated paraffins. (MCCP) to include uses in PVC as well as other substances that contain chloroalkanes with carbon chain lengths within the range C14 to C17.
2022	UK	UK Gov	UK has proposed to enlist MCCPs under the Stockholm Convention as Persistent Organic Pollutants (POPs) [57,58]
2020	Australia	The Australian Department of Health published a hazard assessment	MCCPs meets the domestic PBT criteria, and that some congener groups may meet the Annex D screening criteria for Persistent Organic Pollutants under the Stockholm Convention.[59]
2019	Canada	Canadian Environmental Protection Act, 1999	Canada classified medium-chain chlorinated paraffins as toxic substances under paragraph 64 (a) and 64 (c) of the Canadian Environmental Protection Act, 1999. [60]
2015	United states	US EPA	USEPA regulating medium-chain chlorinated paraffins (MCCPs) under TSCA's new chemical review program. Detailed risk assessment has been performed under TSCA 5 new chemical review program.[61]
India	No Regulation		

Alternatives:

- Aluminium hydroxide, Aluminium phosphate, Zinc Borate and Antimony Trioxide containing compound as flame retardant.
- Natural animal and vegetable oils in Leather production.
- Alkylphosphates and Sulfonated fatty-acid esters.
- Polyacrylic esters, diisobutyrate and phosphates in paint and coating.[62]
- Calcium-Zinc Stabilizers, Barium-Zinc Stabilizers, Organic Tin Stabilizers and Mixed Metal Stabilizers (e.g., Ba/Cd/Zn, Ca/Na/Zn) stabilizers.
- Triethyl Citrate, Diisononyl Cyclohexane-1,2-dicarboxylate, Diisononyl Adipate as plasticisers.

Exposure of MCCPs through food, water, soil and wildlife, by inhalation from from air stacks emission. MCCPs can enter the environment through various pathways, such as release during manufacturing, use, and disposal.

LONG-CHAIN CHLORINATED PARAFFINS (LCCPs):

The term long-chain chlorinated paraffin covers a large group of compounds that vary in terms of carbon chain length (C≥18), uses, and physicochemical and ecotoxicological properties.

Applications:

The restrictions on Short-Chain Chlorinated Paraffins (SCCPs) and Medium-Chain Chlorinated Paraffins (MCCPs) have led to increased usage of Long-Chain Chlorinated Paraffins (LCCPs) as an alternative.

- LCCPs are used as extreme pressure additives and lubricants in metalworking fluids, including cutting oils, metal-forming lubricants, and hydraulic fluids.
- As plasticizers in various polymer products, particularly PVC (polyvinyl chloride) and other flexible plastics.
- As a flame-retardant in PVC products, such as wire and cable insulation, flooring, plastic products, automotive parts, vinyl upholstery and textiles.
- LCCPs are used as additives in paints, coatings, and sealants to enhance their adhesion, moisture resistance, and durability.
- LCCPs are utilized in the leather and textile industries as fat liquors and waterproofing agents.

Routes of Human Exposure:

Routes of exposure for LCCPs are similar to those of MCCPs exposure; however, the level of exposure is different. (**Figure 10**)

Inhalation of LCCP vapors or particles can irritate the respiratory tract, leading to symptoms such as coughing, wheezing, or shortness of breath.

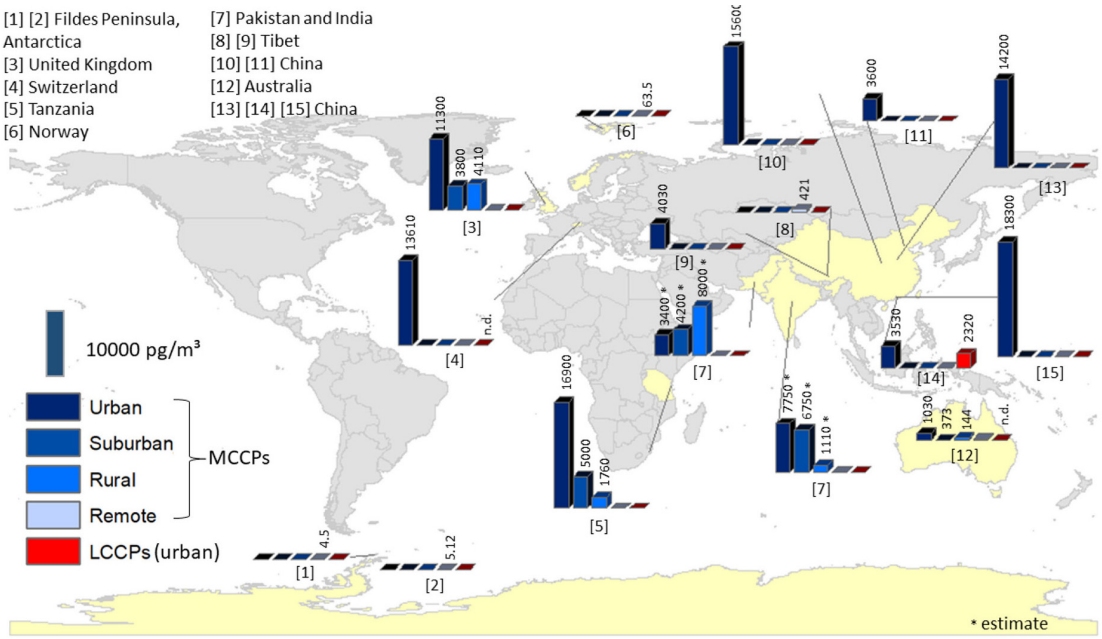


Figure 10: Global air concentrations (pg/m3) of MCCPs (urban, suburban (including subrural), rural, and remote) and LCCPs. (ND: Not Detected).

(Source: South et.al., 2022 https://www.sciencedirect.com/science/article/pii/S0048969722041912)

Health Impact on Exposure

- Direct contact with LCCPs may cause slight skin irritation, dermatitis, or sensitization.[63]
- Inhalation of LCCP vapors or particles can irritate the respiratory tract, leading to symptoms such as coughing, wheezing, or shortness of breath.
- Animal studies suggest that exposure to high levels of chlorinated paraffins may lead to systemic toxicity, affecting organs such as the liver, kidneys, and nervous system.[64], [65]
- Prolonged exposure to high levels of chlorinated compounds may increase the risk of certain types of cancer, although direct evidence for LCCPs is lacking.[66]

Global Regulations on LCCPs

The regulatory status of Long-Chain Chlorinated Paraffins (LCCPs) varies globally. **Table 5** presents the various regulatory statuses and actions taken by different countries for the management of Long-Chain Chlorinated Paraffins (LCCPs).

Table 5: Regulatory status of LCCPs

Year	Country	Regulation	Remark
2022	European Union	ECHA	ECHA is regulating long-chain chlorinated paraffins (LCCPs) REACH regulation, which mandates registration, evaluation, potential authorization, and restriction of LCCPs based on their hazardous properties and usage within the European Union.
2019	Canada	Canadian Environmental Protection Act, 1999	Canada classified Long-chain chlorinated paraffins as toxic substances under paragraph 64 (a) and 64 (c) of the Canadian Environmental Protection Act, 1999. [67]
2016	United States	US EPA	EPA is regulating LCCPs SNURs, under TSCA section 5(a)(2), (vLCCPs—alkyl chain length of C21 and above)[68]
India	No Regulation		

Alternatives

Presently there are many alternatives to LCCPs, some of them are listed below:

- Alkanol amides (e.g., 2:1 di-ethanolamine (DEA) tall oil fatty acid alkanol amide)
- Isopropyl oleate
- Nitrated compounds (e.g. Doverlube NCEP-nitrogen-containing compound)
- Overbased calcium sulphonates
- alkyl phosphate esters
- Phenol, isopropylated, phosphate (ITAP) (3:1)
- Tributyl phosphate (TBP)
- Triaryl phosphate
- Sulphurized polyisobutene, polypropylene and polystyrene.
- Polyolefin sulphide

ENDNOTES

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