

Environmental Impact of Chlorinated Paraffin Contamination

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SUMMARY

Chlorinated paraffins (CPs), or polychlorinated alkanes (PCAs), are chlorinated derivatives of n-alkanes classified into short, medium, and long chains (C10–C30) with chlorine content ranging from 40–70%. These stable, non-flammable, and water-insoluble compounds resemble persistent organic pollutants (POPs) like PCBs but have received less attention due to lower toxicity and limited environmental data. First synthesized in 1858 and mass-produced by 1932, CPs are widely used as plasticizers, flame retardants, and additives in adhesives, paints, rubbers, and metalworking fluids. CPs dissolve in chlorinated solvents and hydrocarbons but degrade under heat and light. CPs enter the environment through industrial activities, product disposal, leaching, runoff, and volatilization. Lower chlorinated CPs are more mobile, transferring between air, water, sediment, and soil. They bioaccumulate in organisms, particularly top predators like sharks and marine mammals, with significant trophic magnification observed in marine ecosystems like the East China Sea.

INTRODUCTION

Chlorinated paraffins are chlorinated derivatives of paraffinic hydrocarbons. They are referred as polychlorinated alkanes (PCAs) because they are produced by chlorination of n-alkane feedstocks. Commercial PCA mixtures fall into different categories: C10–C13 (short), C14–C17 (medium) and C20–C30 (long). These mixtures are further subcategorized into their weight content of chlorine: 40–50%, 50–60%, and 60–70%. CPs are viscous, colorless or yellowish dense oils with low vapor pressures, except for those of long carbon chain length with high chlorine content (70%), which are solid. CPs are practically insoluble in water, lower alcohols, glycerol and glycols, but are soluble in chlorinated solvents, aromatic hydrocarbons, ketones, esters, ethers, mineral oils and some cutting oils. They are moderately soluble in unchlorinated aliphatic hydrocarbons. Knowledge of the environmental chemistry of PCAs is needed because the physical properties of short and medium chain mixtures are similar to those of the persistent organic pollutants or POPs (PCBs, DDT, toxaphene etc). PCAs have received much less attention in terms of exposure and risk assessment than the POPs because of lower mammalian toxicity than most POPs and the lack of environmental measurements for estimating human and animal exposure.

Development of CPs

The first documented synthesis of chlorinated paraffins was performed in 1858 by the Swiss researcher Pompejus Bolley. Through extensive chlorination of a molten paraffin, he gained viscous liquids with chlorine contents between 36 and 61 weight-% Cl. Higher chlorination degrees were difficult to obtain due to a noticeable increase in viscosity. Bolley could not further determine the composition of these complex mixtures, and proposed to name the product “chloraffin”. Although Bolley mentioned the potential use of “chloraffin” as an impregnating agent, his findings were overlooked until 1880. During this period, patents were published which suggested the use of CPs in waterproofing of textiles, for the improvement of water binding properties in cosmetics, and (in admixtures with tung oil) in transparent or opaque glaze films. Accordingly, a small-scale industrial CP production may already have begun at the end of the 19th century.

The first large scale usage of PCAs began in 1932 when they were incorporated as extreme pressure additives in lubricants. Global consumption estimates for 1993 were reported to be 300 kt/year. In the United States and in Canada consumption estimates are reported to be 44–45 kt/year and 3.5–5 kt/year, respectively. In Europe, annual consumption ranges from 100 kt to 200 kt. Production in the US, Europe, and Japan, the major

consumers of chlorinated paraffins globally, remained relatively constant throughout the 1990s. In recent years, China has become the world's main CP producer, and most new patents on CPs are claimed in this country.

Application

Common applications of PCAs include high temperature lubricants, plasticizers, flame retardants, and additives in adhesives, paints, rubber, and sealants. A major use of PCAs is as extreme temperature additives in metal working fluids (short, medium, and long carbon chain length compounds of 50–60 wt% Cl) for a variety of engineering and metal working operations such as drilling, machining/cutting, drawing, and stamping. The PCA content of the metal working fluid usually ranges from 2% to 10%, but can be up to 80% or more for specialty applications. PCAs (typically medium carbon chain length compounds of 50–60 wt% Cl) are also used as secondary plasticizers for polyvinyl chloride (PVC) and in other plastics (polyesters, polyolefins, polystyrene) and rubbers (neoprene). PCAs can partially replace primary plasticizers such as phthalates and phosphate esters. As plasticizers, PCAs lend flame retardancy to the product, unlike phthalate esters. They are added prior to the processing step for the polymer. PCAs did not replace PCBs in the late-1970s, despite having some similarities in physical properties and flame retardant characteristics. PCAs were not good PCB replacements for uses requiring high heat stability (e.g., capacitors, transformers) because of their much lower thermal stability.

Physico chemical properties of PCA

Chlorinated paraffins that have been manufactured from pure n-paraffins are generally unreactive and stable during storage at normal temperatures. Depending on their chain length and degree of chlorination, chlorinated paraffins are colourless or yellowish, mobile to highly viscous liquids or wax to glassy solidified substances. Chlorinated paraffins are practically insoluble in water but can form emulsions or suspensions in certain conditions. They are also non-flammable and exhibit low volatility, making them suitable for various industrial applications. Chlorinated paraffins are generally stable under normal storage conditions but can undergo dehydrochlorination when exposed to heat and light, especially in the presence of metals like aluminium or zinc.

Routes of Environmental release

PCAs can enter the environment through various pathways, including during manufacturing, storage, transportation, industrial use, or product disposal. Environmental release may also occur due to their use in products like plastics, paints, and sealants, or through processes such as leaching, runoff, or volatilization from landfills, soils treated with sewage sludge, and other waste disposal sites. Most discharges are linked to manufacturing and industrial activities. Waterborne PCA releases from industrial facilities may result from spills or cleaning activities, such as reactor vessel wash-downs. Notably, the release of waterborne C10-C13 PCAs is largely attributed to industrial usage. Inappropriate disposal of used metalworking lubricants, storage drums, and residues from workpieces can also contribute to environmental contamination. Additionally, reconditioning of used drums by repair businesses may pose risks to the environment. Another significant pathway is through the disposal and incineration of waste containing PCAs. When products like plastics, textiles, painted materials, paint cans, and oils are landfilled, slow leaching or volatilization of PCAs may occur. However, releases from embedded materials are expected to be minimal due to the low vapor pressure and water solubility of PCAs.

Environmental Contamination

Releases occur during production, storage, transportation, use, recycling and disposal of CPs, as well as CP containing products. Even in countries where SCCPs are banned, they are still being released into the environment from old materials that remain in use or have been disposed. A particular important pathway of CPs to the environment is the release of sludge and effluents from sewage treatment plants (STPs). Especially lower chlorinated SCCPs (e.g. Cl₅₋₆) may have a potential to pass more easily through the STP treatment, as a relatively higher abundance of Cl₅₋₆ SCCPs was found in effluent and lake water compared to that in the influent and sewage sludge. Other CP release pathways include leaching, runoff or volatilization from landfills, facility wash-downs and burning of waste.

CPs can transfer between air, water, sediment and soil, as well as organisms, and have the potential to accumulate in both abiotic and biotic phases. SCCPs with a shorter carbon chain length and lower chlorine content are more prone to volatilization and migration compared to longer chained CPs, which have a greater affinity for particulates in water and air. As hydrophobic compounds, CPs are less likely to be present in water at

high concentrations. However, SCCPs have been detected in marine waters near point sources of Bohai Sea, China at concentrations of 4.1-13.1 ng/L. Relatively high concentrations were also reported in urban snow (SCPs 330-3200 ng/L), reflecting the ability of snow to accumulate pollutants emitted from human activity and to act as a temporary storage of contaminants. Decreasing SCCPs concentrations from the coast to the open ocean were observed in China, suggesting that riverine input can be an important source of SCCPs. Due to their strong sorption to organic matter, the main fraction of CPs in water is typically sorbed to suspended matter rather than freely dissolved.

Bioaccumulation of CPs

Since 2010, SS/MCCPs concentrations in biota have been reported mainly from China with a focus on aquatic species. Among the different species investigated, relatively high concentrations were reported in sharks (SCCPs 55-5200 ng g⁻¹ lw) and marine mammals (e.g. dolphins and porpoises; SCCPs 570-24,000 and MCCPs 670-56,000 ng g⁻¹ lw), indicating that, similar to POPs, animals that are high in the food chain and have long life spans have the potential to accumulate higher concentrations of CPs. Furthermore, SS/MCCPs concentrations observed in near shore/estuarine marine mammal species (e.g. humpback dolphins) were 2-3 times higher compared to those with habitats further offshore.

CPs (sum of SCCPs and MCCPs) in benthic organisms and fish from various rivers in the UK ranged from < 0.05 to 0.8 and < 0.1 to 5.2 µg/g ww, respectively.

The bioaccumulation and trophic magnification of Short-chain chlorinated paraffins (SCCPs) has been studied in the East China Sea (ECS). SCCP concentrations ranged from 12.5–242 ng/L in seawater and 12.8–1819 ng/g wet weight in marine organisms, with C10-11 and Cl 5-7 homologues dominating. The trophic magnification factor (TMF) for SCCPs was 3.98, indicating significant trophic magnification in the ECS food web.

CONCLUSION

The availability of high amounts of chlorine, the cheap production of CPs and, last but not least, the various fields of bulk applications in a situation without any restrictions on the use of MCCPs and LCCPs has led to an unmatched production of these industrial chemicals in many countries worldwide. Various industrial CP products of different composition, each with a huge variety, and substantial difficulties in the quantitative analysis of CPs and the understanding of metabolisms and toxicology have hampered the exact assessment of the environmental dimension of this complex substance class. The high production volume gives rise to an incomparable discharge into the environment, which will exceed all other POPs – if CP production continues on the current high level. The persistence and low degradation rates of CPs contribute to their long-term impact, affecting trophic chains and ecosystems. Monitoring and regulation are essential to mitigate these risks. Efforts to replace CPs with less harmful alternatives, coupled with stricter international controls under frameworks are necessary to protect marine biodiversity and ensure ecosystem health.

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