Short-Chain Chlorinated Paraffins: Production, Use and International Regulations

Heidelore Fiedler

Abstract Chlorinated paraffins (CPs) are a group of synthetic organic chemicals consisting of *n*-alkanes with varying degrees of chlorination, usually between 40 and 70% by weight. There are no known natural sources of CPs. CPs are produced by chlorination of *n*-alkane feedstocks. CPs typically are viscous oils with low vapor pressures; they are practically insoluble in water but are soluble in chlorinated solvents or mineral oils. They are toxic to wildlife, long-lasting in the environment and build up in the tissues of organisms. Long-chain CPs are believed to be much less toxic to aquatic life than the related short- or medium-chain CPs.

CPs consist of extremely complex mixtures allowing many possible positions for the chlorine atoms. Depending on the degree of chlorination, they are grouped into low (<50%) and high (>50%) chlorine containing. Depending on the chain length, the products are often subdivided into short-chain (C_{10}–C_{13}), medium-chain (C_{14}–C_{17}) and long-chain (C_{18}–C_{30}) CPs.

CPs, including short-chain chlorinated paraffins (SCCPs), are used worldwide in a wide range of applications such as plasticisers in plastics, extreme pressure additives in metalworking fluids, flame retardants and additives in paints. Their wide industrial applications probably provide the major source of environmental contamination. CPs may be released into the environment from improperly disposed metalworking fluids containing CPs or from polymers containing CPs. Loss of CPs by leaching from paints and coatings may also contribute to environmental contamination. The potential for loss during production and transport is expected to be less than that during product use and disposal. Despite many efforts, a global picture as to the definition of CPs, present production, uses and occurrences is still not yet obtained.

Since about 20 years, SCCPs have become subject to regulation at national and international level due to their physical–chemical properties and adverse effects.

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Action has been initiated for severely restricting or banning production and use of certain CPs. The latest activities include the listing of SCCPs under the Persistent Organic Pollutants (POPs) Protocol of the United Nations Economic Commission for Europe (UNECE) Longe-Range Transboundary Air Pollution Convention and ongoing discussions on including SCCPs to the Stockholm Convention on POPs.

Keywords Chlorinated paraffins, Definitions, Regulation, Risk assessment, Releases

Contents

Abbreviations

ACP	Arctic contamination potential
b.w.	Body weight
CAS	Chemical Abstract Service
COP	Conference of the parties
CP(s)	Chlorinated paraffin(s)
CSTEE	European Scientific Committee on Toxicity, Ecotoxicity and the Environment
CTV	Critical toxicity value
E(E)C	European (Economic) Commission
EEV	Estimated exposure value
EINECS	European Inventory of Existing Chemical Substances

EPER	European Pollutant Emission Register
E-PRTR	European Pollutant Release and Transfer Register
GMP	Global monitoring plan
HELCOM	Helsinki Commission
HLC	Henry's law constant
IARC	International Agency for Research on Cancer
IPCS	International Programme on Chemical Safety
IUPAC	International Union for Applied Chemistry
LCCPs	Long-chain chlorinated paraffins
LOAEL	Lowest observed adverse effect level
LOEC	Lowest observed effect concentration
LRTAP	Long-range transboundary air pollution
MAP	Mediterranean Action Plan
MCCPs	Medium-chain chlorinated paraffins
NOAEL	No adverse effect level
OECD	Organisation for Economic Co-operation and Development
OSPAR	Oslo-Paris Convention for the Protection of the Marine Environment of the North-East Atlantic
PARCOM	Paris Commission
PBT	Persistent, bioaccumulative and toxic
PEC	Predicted environmental concentration
PNEC	Predicted no-effect concentration
POPRC	Persistent Organic Pollutants Review Committee
POPs	Persistent organic pollutants
PVC	Polyvinylchloride
RAR	(European) Risk Assessment Report
RQ	Risk quotient
SCCPs	Short-chain chlorinated paraffins
STP	Sewage treatment plant
TDI	Tolerable daily intake
UNECE	United Nations Economic Commission for Europe
UNEP	United Nations Environment Programme
WFD	Water Framework Directive
WHO	World Health Organisation

1 Background

Chlorinated paraffins (CPs) or chlorinated *n*-alkanes are a group of synthetic compounds produced by the chlorination of straight-chained paraffin fractions. The feedstock used determines the carbon chain length distribution of the product. The carbon chain length of commercial CPs is usually between 10 and 30 carbon

atoms, and the chlorine content is usually between 40% and 70% by weight. In general, there are three different carbon-chain length feedstocks that are used to manufacture CPs: short-chain (C_{10}–C_{13}), medium-chain (C_{14}–C_{17}) and long-chain (C_{18}–C_{30}).

Short-chain (SCCPs), medium-chain (MCCPs), and long-chain (LCCPs) CPs all have industrial applications and similar environmental concerns. 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 [1].

They tend to be oily liquids or waxy solids and they are toxic to wildlife, long-lasting and build up in the tissues of organisms. LCCPs are believed to be much less toxic to aquatic life than the related SCCPs and MCCPs [2].

Briefly, LCCPs and MCCPs occur as complex mixtures; they are waxy solids that decompose at over 200°C with the release of hydrogen chloride gas. They are virtually insoluble in water but dissolve fully in most non-polar organic solvents like paraffin oil. They are non-flammable and do not evaporate easily. The main use of LCCPs and MCCPs is as plasticisers in flexible polyvinylchloride (PVC), industrial metalworking fluids used in processes involving cutting, drilling, machining and stamping metal in engineering and manufacturing. Because of their fire retarding properties, they are sometimes added to rubbers for particular applications. They are also used in paints and other coatings, leathers, textiles and sealing compounds.

CPs are non-biodegradable and are bioaccumulative. They have been detected in marine and freshwater animals and in sediments in industrial areas and have also been found in remote locations. They are toxic to aquatic life.

SCCPs and MCCPs are a priority for risk assessment under the Council Regulation EEC 793/93 of 23 March 1993. CPs are candidates for selection, assessment and prioritisation under the OSPAR strategy and priority chemicals under the European Water Framework Directive (WFD).

SCCPs are mainly used in metalworking fluids, in sealants, as flame retardants in rubbers and textiles, in leather processing and in paints and coatings. SCCPs having carbon chain lengths of between 10 and 13 carbon atoms have a degree of chlorination of more than 48% by weight. Commercially available C_{10}–C_{13} CPs are usually mixtures of different carbon chain lengths and different degrees of chlorination, although all have a common structure, in that no secondary carbon atom carries more than one chlorine atom.

Since SCCPs are highly toxic to aquatic organisms, they do not break down naturally and tend to accumulate in biota. Because of their persistence, bioaccumulation, potential for long-range environmental transport and toxicity, they are classified as persistent organic pollutants (POPs) and either listed or under consideration for listing in international agreements at regional or global level.

Although the Stockholm Convention on POPs is the latest of the international agreements, its global coverage and inclusion of all environmental media makes the Stockholm Convention the most important of these. However, in the other regional Conventions, a lot of experiences have been gained, which are used in the proposal to list SCCPs as new POPs in one of the annexes to the Stockholm Convention.

This chapter focuses on SCCPs with an emphasis on production, uses and international regulation.

2 Identity, Production, Toxicity, Fate and Transport of SCCPs

2.1 Industrial Production

At industrial scale, CPs are produced through chlorination of a petroleum-based hydrocarbon stream that has a distribution in carbon chain lengths. Individual chlorinated alkanes are typically not considered as CPs by the chemical industry. When a specific description is given for commercial CPs, it can be expected that the mixture will fall, on average, within that description, but other compounds may be present. Theoretically, SCCPs with the chemical formula $C_xH_{(2x-y+2)}Cl_y$, where x = 10–13 and $y \geq 1$, may contain a chlorine content ranging from 16% to 87% by weight. However, not all possible congeners would be produced in the industrial manufacturing process. For example, a product described as SCCP, 40% chlorine, will, on average, be composed of chlorinated alkanes that are 40% chlorine by weight and contain predominantly chain lengths between 10 and 13 carbons; the product may also contain lower and higher chlorinated alkanes as impurities. Currently, it is estimated that there are essentially no alkanes with <30% chlorination being produced and likely none with greater than 75% chlorination [3].

2.2 SCCP Definitions and Their Relationship to CAS Numbers

The numbers provided by the Chemical Abstracts Service (CAS) [4] are the unanimously accepted definitions for chemical substances. Given the complexity of this class of substances, an exhaustive listing of CAS numbers is not possible. Nevertheless, the following information contained in Table 1 provides a partial list of CAS numbers that contain chlorinated alkanes that fall within the defined range of SCCPs.

In addition, some CAS numbers denote individual chlorinated alkanes, not mixtures. Examples of these are in Table 2.