

LEARNING TOXICOLOGY THROUGH OPEN EDUCATIONAL

SHORT-CHAIN

CHLORINATED



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INTRODUCTION

Short-chain chlorinated paraffins (SCCPs) are chlorinated derivatives of aliphatic hydrocarbons n-alkanes, which show high persistence, bioacumulative and toxic properties (PBT). Chlorinated paraffins were first produced commercially in the 1930s and used as plasticizers (in paints, rubber, polyvinyl chloride), flame retardants, lubricating oils, as additives (in metal working fluids and sealants), etc. (EPA, 2009). SCCPs have been widely studied, due to their relatively high assimilation and accumulation potential in environment and living organisms. Releases of SCCPs may occur during production, storage, transportation, industrial use, disposal and burning of waste. By incineration of chemical products or wastes containing SCCPs can result PCBs and PCNs. The worldwide release of SCCPs from production and use was between 1935 and 2012: (a) to air (1690–41,400 t), (b) to surface water (1660–105,000 t), (c) to soil (9460-81,000 t). In present, the global production of total SCCPs exceeds 1 million t/year. China is now the largest CP producer and consumer in the world. (Glüge et al., 2016). SCCPs are the most concerning regarding environmental distribution and potential persistence in different matrices, bioaccumulation, and toxic properties (Friden et. al., 2011, Stockholm Convention, 2016) recognized the PBT properties and long-range transport potential of SCCPs and evaluates a possible global restrictions program.

STRUCTURE AND PROPERTIES OF SCCPs

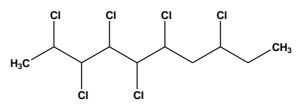
Technical SCCPs mixtures consist of thousand components (Serrone et al. 1987) and, due to the large number of isomers, is difficult to provide analytical methods for their quantitative analysis.



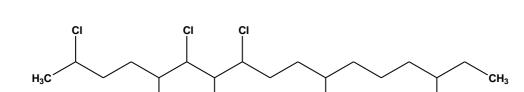
TOPIC 4.3: Persistent organic pollutants *(POPs) UNIT 2.-* Short-chain chlorinated paraffins (SCCPs)



Short chain chlorinated paraffins (SCCPs) are chlorinated derivatives of *n*-alkanes, having 10 to 38 carbon atoms in their structure and a chlorine content between 30% to 70% by weight. The SCCPs vary in their chain lengths, the degree of chlorination and distribution in the environment. Based on the chain lengths SCCPs are divided into three main categories, *short- (C10 - C13), medium- (C14 - C17) and long-chain (C18 - C30.* Taking into account their degree of chlorination SCCPs are: low (< 50%) and high (> 50%) clorinated (Tomy et al., 2000).



2,3,4,5,6,8-hexachlorodecane, an example of a short-chained chlorinated paraffin (61% Cl by weight)



2,5,6,7,8,11,15-heptachloroheptadecane, an example of a medium-chain chlorinated paraffin (52% CI by weight)

In Table 1 are presented some physical-chemical properties of SCCPS

Due to their vapour pressure (values $(2.8 \times 10^{-7} \text{ to } 0.5 \text{ Pa})$, SCCPs are compounds known to undergo long-range atmospheric transport (LRAT). The values of Henry's law constants for C10–12 SCCPs are similar to those of some chlorinated pesticides (hexachlorocyclohexane, toxaphene) and determine partitioning from water to air or from moist soils to air, depending on the environmental conditions and concentrations. The melting points of SCCPs increases with increasing carbon chain length and with increasing of chlorine





content. At room temperature, SCCPs (with 40% chlorine) are colourless to yellowish liquids, and white solids (at 70% chlorine) with (softening point about 90°C).

Table 1	Polovant	nh	veical-chomical	nronortios
	Relevant	рп	ysical-chemical	properties

Property	Value
Vapour pressure (Pa)	0.028 to 2.8 x 10 ⁻⁷ Pa
	0.021 Pa at 40 °C (SCCP with 50% chlorine
	1.4 x 10 ⁻⁵ to 0.066 Pa at 25°C (SCCP with 50-60% chlorine)
Henry's Law Constant (Pa·m ³ /mol)	0.7 - 18 Pa x m ³ /mol
Water solubility (µg/L)	400 - 960 µg/L, (C10-C12 chlorinated
	mixtures)
	6.4 - 2370 μg/L ,C10 – C13 chlorinated mixtures)
	150 to 470 μg/L, at 20°C, (SCCPs with 59% chlorine
log K _{OW}	4.48 - 8.69
	4.39-5.37, (SCCPs with 49-71% chlorine)
log K _{OA}	4.07 - 12.55, (SCCP with 30-70% chlorine)
	(modelled values)

Source: Stockholm Convention, 2016

SCCPs have very low solubilities in water, ranging from 22.4 to 994 mg/L for some of the short-chain mixtures. Log of octanol/water partition coefficients (Kows) for SCCPs are from 5.85 to 7.14 (Tomy et al. 2000; Hilger et al. 2011). The very low solubility in water and low vapour pressure of SCCPs determine their low mobility in environment. The monitoring data from Sweden and the UK indicate low levels of contamination in water sediments, aquatic and terrestrial organisms, commercial foods and some air dispersion (Government of Canada, 2009).

PERSISTENCE OF SCCPs

PERSISTENCE IN AIR

Because their atmospheric half-lives are greater than 2 days, SCCPs are generally considered persistent and classifyed having the potential for long-



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range transboundary atmospheric transport (LRTAP) (Stockholm Convention, 2016). They also can be transported as suspended particles in the water and dust particles in the air. SCCPs were detected in individual samples of air collected at Islands in the high Arctic in concentrations ranged from 1 to 8.5 pg/m³ in gas-phase samples(). Although SCCPs do not degrade by direct photolysis in air, they would be subject to attack via hydroxyl radicals in the troposphere (Koh and Thiemann, 2001).

PERSISTENCE IN WATER

In the aqueous phase, rates of hydrolysis, photolysis with visible or near UV radiation, oxidation and volatilization are insignificant at ambient temperatures. Studies have shown that degradation by microorganisms is possible, due to the ability of aerobic microorganisms to oxidize chlorinated paraffins, depending on their acclimatization, the chain length and degree of chlorination (Hilger et al., 2011; Government of Canada 2009). SCCPs are not expected to degrade significantly by abiotic processes such as hydrolysis. Koh and Thiemann showed that SCCP mixtures underwent rapid photolysis in acetone–water with half-lives of 0.7–5.2 hours. The half-life of a 52% chlorine by weight SCCP in pure water, under the same conditions, was 12.8 hours and photoproducts included n-alkanes..These results suggest that sunlight photolysis may be a significant degradation pathway for some SCCPs.

PERSISTENCE OF SCPCs IN SOIL AND SEDIMENT

SCCP residues were found in the surficial sediments of the Arctic lakes g/g dry wt.): 4.5) and (17.6. Concentration of SCCP residues in sediments from Lakes Winnipeg, Manitoba, and Yukon, indicated that residues were present in the slices dated 1947. SCCP residues in sediments observed in the Lake Ontario dated from1949. The fact that SCCP residues were detected in sediment dating back to the 1940s is evidence that SCCPs can persist for long periods in sediment. (Muir et al. 2000; Stockholm Convention, 2007).





BIOACCUMULATION OF SCCPs

The presence of SCCPs was reported in the blubber from Artic Islands, whales and walrus from Greenland at concentrations ranging from 199 to 626 ng/g wet wt. It was observed that the concentration profiles for the Arctic marine mammals show a predominance of the shorter carbon chain length congeners C10 and C 11 (Tomy et al., 2000). Individual SCCPs congeners had half-lives in trout (7 to 53 days), shorter than those for PCB congeners in studies under the same conditions (Muir et al. 2000). Bioaccumulation factors (BAFs) for SCCPs homologue groups in western Lake Ontario in trout were 114 to 444 days (see Table 2).

Table 2.	Bioaccumulation	factors	for	SCCPs	in	lake	trout	of	western	Lake
Ontario										

Homologue	Concentration in water (ng/l)	Concentration in lake trout ^a <i>a</i> ng/g wet weight	BAFww
C10	0.16	3.4	21 250
C11	0.48	18.3	38 125
C12	0.98	33.6	34 286
C13	0.09	10.3	114 444
∑C10–C13	0.18	65.7	36 500

^a Concentrations in whole fish (wet weight), Source: Muir et al. 2000.

Chlorinated dodecanes (C12) are the most present SCCPs in lake water and fish. The highest BAFs are seen for the tridecanes (C13). The overall BAF for SCCPs (C10–13) in lake trout from western Lake Ontario is 36 500. Reported bioconcentration factors (BCFs) for SCCPs vary among different species, ranging from <1 in marine algae to 140 000 in the common molluscs. Log octanol/water partition coefficients (Kows) for SCCPs vary in fish and molluscs from 5.06 to 8.12. (Tomy et al., 2000).





SOURCES OF HUMAN EXPOSURE

Chlorinated paraffins (including SCCPs), are not known to occur naturally (Government of Canada, 2009). The two major sources of release of SCCPs into the environment are during their production and their use. During production, most emissions are to wastewater and to air and can reach the marine environment via rivers and atmosphere. SCCPs occur were sediments and surface waters in rivers, lakes, seas, air and soil spread with sewage sludge Stockholm Convention, 2016). SCCPs were the second most abundant group of compounds measured in indoor air of homes in France (concentration of 45 µg g-1 dust (Bonvallot et al., 2010). The main environmental source of human exposure is food and, to a lesser extent, drinking-water (Harada et al., 2011). Levels in food of 30 to several thousand µg/kg SCCPs have been measured In carp (Hamilton Harbour) and trout (Lake Ontario and Michigan River) (Tomy et al. 2000; Houde et al., 2008). The presence of SCCPs in Arctic environmental samples and remote terrestrial samples is mainly due to LRTAP. The EU assessment (European Commission, 2005) considered a human uptake value of 20 µg/kg bw per day a reasonable worst-case value.

HUMAN HEALTH IMPLICATION RELATIVE TO SCCPs

Health hazard

The majority of human exposure to SCCPs is from food consumption and from some exposure resulting from inhalation and dermal contact (Stockholm Convention, 2016). Limited information regarding the toxicokinetics of SCCPs correlated with chain length and degree of chlorination and oral exposure are available. Absorption (up to about 60%) occurs by oral administration, high absorption being correlated with low chlorinated compounds. Absorbed SCCPs are distributed to tissues of high metabolic activity and/or high rate of cell proliferation following oral dosing. Comparing with other chlorinated compounds (PCBs, pesticides, etc.), SCCPs exhibit less acute and chronic toxic effects,





lower reproductive and embryotoxicity in birds and mammals (Tomy et al., 2000).

The risk profile documents on human health and environment associated with SCCPs reports that they are very toxic to aquatic organisms. SCCPs can cause toxicological effects in mammals and may affect the liver, the thyroid hormone system and the kidneys, by causing thyroid hyperactivity, which in the long-term can lead to carcinogenicity in these organs. SCCPs are also classified as suspected of causing cancer, and are listed as category 1 endocrine disrupters for human health. In 2009 EPA, recommended that daily doses of SCCPs for the general population should not exceed 11 μ g/kg bw for prootection against neoplastic effects.

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