LEARNING TOXICOLOGY
THROUGH OPEN EDUCATIONAL

LYHYTKETJUISET KLOORATUT PARAFIINIT (SCCP)

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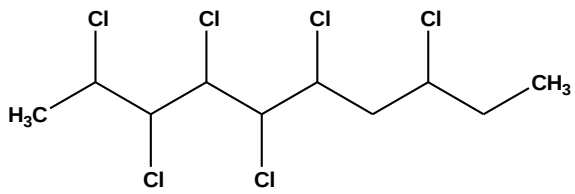
JOHDANTO

Lyhytketjuiset klooratut parafiinit (SCCP) ovat alifaattisten hiilivetyjen n-alkaanien kloorattuja johdannaisia, joilla on erittäin pysyviä, bioakkumuloituvia ja myrkyllisiä ominaisuuksia (PBT). Kloorattuja parafiineja valmistettiin ensin kaupallisesti 1930-luvulla ja niitä käytettiin pehmittiminä (maaleissa, kumissa, polyvinyylikloridissa), palonestoaineina, voiteluöljyinä lisäaineina (metallintyöstönesteet ja tiivisteet) jne. (EPA, 2009). SCCP-yhdisteitä on tutkittu laajalti, koska niiden suhteellisen korkea assimilaatio ja kertyvyyspotentiaali ovat ympäristössä ja elävissä organismeissa. SCCP-yhdistepäästöjä voi esiintyä tuotannon, varastoinnin, kuljetuksen, teollisen käytön, jätteen hävittämisen ja palamisen aikana. Polttamalla kemiallisia tuotteita tai SCCP-yhdisteitä sisältäviä jätteitä voi syntyä PCB- ja PCN-yhdisteitä (polyklooratut naftaleenit). Väkevien kloorattujen parafiinien maailmanlaajuiset päästöt tuotannosta ja käytöstä olivat vuosien 1935 ja 2012 välillä: (a) ilmaan (1690-41 400 t), (b) pintavesiin (1660-105 000 t), (c) maaperään (9460-81 000 t). Nykyisin kokonaisvalvontakomponenttien maailmanlaajuinen kertyminen ylittää miljoona tonnia vuodessa. Kiina on nyt maailman suurin CP-tuottaja ja kuluttaja. (Glüge et ai., 2016). SCCP-yhdisteet ovat kaikkein huolestuttavimpia ympäristösaasteita ja ne säilyvät potentiaalisena eri ympäristöissä, ne kertyvät ja niillä on myrkyllisiä ominaisuuksia (Friden et al., 2011, Tukholman yleissopimus, 2016). Nyt tunnustetaan lyhytketjuisten kloorattujen parafiinien PBT-ominaisuudet ja pitkän kantaman kuljetuspotentiaali ja arvioidaan mahdolliset maailmanlaajuiset rajoitukset.

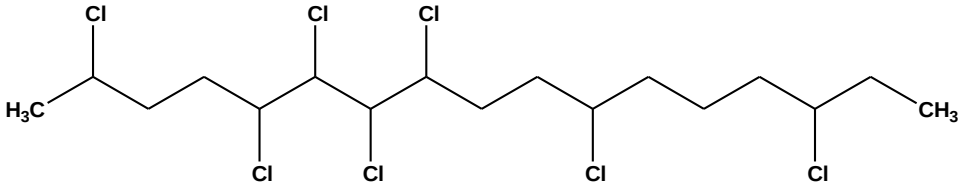
SCCP-YHDISTEIDEN RAKENNE JA OMINAISUUDET

Tekniset SCCP-yhdisteet koostuvat tuhansista komponenteista (Serrone et ai., 1987), ja koska niissä on suuri määrä isomeerejä, on vaikea löytää analyyttisiä menetelmiä niiden kvantitatiiviseen analyysiin.

Lyhytketjuiset klooratut parafiinit ovat n-alkaanien kloorattuja johdannaisia, joiden rakenne on 10-38 hiiliatomia ja kloorin pitoisuus 30-70 painoprosenttia. SCCP:t vaihtelevat ketjun pituuden, kloorauksen ja jakautumisen asteen mukaan ympäristössä. Ketjun pituudet SCCP-yhdisteissä jaetaan kolmeen pääluokkaan, lyhyt (C10 - C13), keskipitkä (C14 - C17) ja pitkä (C18 - C30). Jos otetaan huomioon kloorausaste, luokat ovat alhainen (< 50%) ja korkea (> 50%) klooraus (Tomy et ai., 2000).



2,3,4,5,6,8-heksaklorodekaani, esimerkki lyhytketjuisesta klooratuista parafiinista
(61 paino-% Cl)



2,5,6,7,8,11,15-heptaklooriheptadekaani, esimerkki keskipitkäketjulla olevasta kloratusta parafiinista (52 paino-% painosta)

Taulukossa 1 esitetään SCCP-yhdisteiden fysikaalis-kemiallisia ominaisuuksia.

Höyrynpaineen arvoista (arvot (2,8 x 10-7 - 0,5 Pa) johtuen SCCP:t ovat yhdisteitä, joiden tiedetään osallistuvan pitkän kantaman ilmakehän kuljetukseen (LRAT). Henryn lain mukaisten vaatimusten C10-12-SCCP:n vakioarvot ovat samanlaisia kuin joidenkin kloorattujen torjunta-aineiden

(heksakloorisykloheksaani, toksapeeni) ja määrittävät jakautuminen veden välityksellä ilmaan tai kosteasta maaperiästä ilmaan riippuen ympäristöolosuhteista ja pitoisuuksista. SCCP-yhdisteiden sulamispisteitä kasvavat hiiliketjun pituuden kasvaessa ja klooripitoisuuden kasvaessa. huoneen lämpötilassa SCCP-yhdisteet (40% kloorilla) ovat värittömiä, kellertäviä nesteitä ja valkoisia kiintoaineita (70% kloorilla) (pehmenemispiste noin 90 °C).

Taulukko 1. Keskeiset fysikaalis-kemialliset ominaisuudet

Property	**Value**
Vapour pressure (Pa)	0.028 to 2.8 x 10^{-7} Pa
	0.021 Pa at 40 ºC (SCCP with 50% chlorine)
	1.4 x 10^{-5} to 0.066 Pa at 25ºC (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 20ºC, (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 classified having the potential for long-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/m^3 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 SCCPs 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 SCCPs 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] *a* 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 µg/kg bw for protection against neoplastic effects.

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