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SHORT-CHAIN CHLORINATED PARAFFINS IN BIOTA – LEVELS AND EFFECTS

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ABSTRACT
Short-chain chlorinated paraffins (SCCPs) are highly complex technical mixtures of polychlorinated *n*-alkanes with carbon-chain lengths from C_{10}-C_{13} and chlorine content between 49 and 70%. They are produced by chlorination of n-alkanes and do not occur naturally. Because of their physical properties (viscosity, flame resistance) they are used in many different applications, such as lubricant additives, PVC plasticizers and flame retardants in paints, adhesives and sealants. Among the chlorinated paraffin mixtures, SCCPs have the highest potential for release into the environment, because of their higher vapour pressure and water solubility (about 10-100 times higher than for PCBs).

SCCPs can reach the environment through production, storage or use, as well as through leeching, runoff and volatilization from contaminated areas. Despite the fact that they are one of the most challenging groups of compounds to quantify and analyze, SCCPs have been detected in biota and humans, as well as a variety of environmental matrices such as sediments and air. SCCPs have also been detected in remote places such as the Arctic (Reth *et al.*, 2006) and dated sediment cores, suggesting long-range atmospheric transport and persistence in the environment. SCCPs have been found to be toxic to aquatic and soil organisms, fish and there is some evidence of carcinogenicity. This paper reviews the current state of knowledge and highlights the need for further research in order to improve future monitoring efforts.

KEYWORDS: short-chain chlorinated paraffins, analysis, environmental levels, toxicity.

1. INTRODUCTION

Chlorinated paraffins, also known as polychlorinated *n*-alkanes (PCAs), are a class of industrial chemicals comprising of chlorinated straight chain hydrocarbons. They are produced with free radical chlorination and have a wide range of applications, but are mainly used as extreme pressure lubricant additives, plasticizers, flame-retardants and paint additives (WHO, 1996). Since their introduction in the chemical market in the 1930s, their world production has increased to more than 300,000 t/year. PCAs are designated according to their carbon chain length: short chain chlorinated paraffins (SCCPs, or sPCAs) - $C_{10–13}$; medium chain chlorinated paraffins (MCCPs, or mPCAs) - $C_{14–17}$; long chain chlorinated paraffins (LCCPs) - $C_{18–30}$. In Europe total SSCP production in 1995 was estimated to be ≤ 15 000 tonnes (EC, 2000).

SCCPs are very complex chemicals – commercial formulations contain many thousands of individual molecular structures – which are difficult and challenging to analyze. Sample preparation usually involves extraction and cleanup (by either Soxhlet, Accelerated Solvent Extraction, Liquid Liquid Extraction, Solid Phase Extraction or Solid Phase Micro Extraction) and purification (by either concentrated sulphuric acid treatment, sulphuric acid silica gel chromatography or Gel Permeation Chromatography) (Eljarrat and Barcelo, 2006). GC-ECNI-MS is the most commonly used technique for SSCP analysis in environmental matrices (Lepom *et al.*, 2009). Only two interlaboratory

comparison studies have been conducted for SCCPs (Tomy *et al.*, 1999; Pellizzato *et al.*, 2009). The results of both studies showed great variability, in the older study because of the use of different external standard solutions, and in the most recent one because of differences in detection and calibration methods, confirming the challenging nature of SSCP analysis.

Following their widespread and diverse use, SCCPs can be found in a range of environmental samples, both biotic and abiotic (Tomy *et al.*, 1998b; Muir *et al.*, 2000). However, information on environmental levels is still scarce compared to other persistent organic chemicals (POPs) such as dioxins, PCBs and organochlorine pesticides. The EU has completed a formal environmental and human health risk assessment on SCCPs (UK Environment Agency, 1999). As a result, risk reduction measures have been implemented on SCCPs in Europe from 2004 (EC, 2002). SCCPs have been included in the list of priority hazardous substances of the European Water Framework Directive (EU Directive 200/60/EC). On July 26, 2006, the European Community and its Member States being Parties to the Stockholm Convention nominated SCCPs to be listed in Annexes A, B, or C of the Convention (UNEP/POPS/POPRC.2/INF/6). This paper reviews published data on the levels of SCCPs in the environment and their effects in organisms.

2. ENVIRONMENTAL LEVELS

Considering their low vapour pressure, low water solubility and lipophilic nature, SCCPs are likely to distribute mainly to the soil/sediment phase with little volatilization occurring. They are also likely to be transported as suspended particles in the water, and dust particles in the air (WHO, 1996). Release into the environment may occur during production, storage, usage and disposal of paraffin-containing products, as well as disposal and burning of waste, and land filling of products such as PVC, textiles, painted materials, paint cans and cutting oils (Tomy *et al.*, 1998a). Most releases of SCCPs in wastewater and surface water are expected to be associated with metal working operations, however there is potential for widespread release in small amounts associated with uses in products (e.g. paints, textiles, rubber).

SCCPs have been detected in different environmental matrices. In the atmosphere, SCCPs were detected in samples from the Arctic in concentrations ranging from non-detectable to 8.5 pg m^{-3} in gas-phase samples. In the United Kingdom, Peters *et al.* (2000) reported a mean SCCP concentration of 99 pg m^{-3} in air collected from a semi rural site in Lancaster. In a later study, Barber *et al*. (2005) reported concentrations in the U.K. atmosphere ranging from <185 to 3430 pg m^{-3} (mean of 1130 pg m^{-3}) and were higher than 1997 concentrations measured at the same site. This study also calculated an average concentration of 600 pg m^{-3} of SCCPs in the UK atmosphere.

In sewage sludge concentrations of SCCPs ranged from 6.9 to 200 µg g^{-1} dry weight (Stevens *et al*., 2002), with the highest concentrations being in sludge from industrial catchments. In marine sediments from Barcelona concentrations of SCCPs were much lower than those in the UK, in the range of 0.21 to 1.17 µg g^{-1} dry weight (Castells *et al.*, 2008). In sediments from the North and Baltic Seas SCCPs ranged from 21-172 ng g^{-1} dry weight (Hüttig and Oehme, 2005). A dated sediment core study from Lake Thun in Switzerland revealed a considerable deposition of SCCPs over a period of 30 years, from 1961 to 2004, with SSCP concentrations ranging from 5 to 51 ng g^{-1} (Iozza *et al.,* 2008). A study from Lake Ontario and Lake Michigan has shown their ubiquitous nature and widespread distribution and has revealed biomagnification factors for several SSCP isomers ranging from a 3-fold from rainbow smelt to lake trout, to a 23-fold from *Diporeia* to sculpin (Muir *et al*., 2003). This clearly suggests an increase through the trophic levels in aquatic food webs.

SCCPs have also been detected in marine wildlife, such as beluga (*Delphinapterus leucas*), ringed seal (*Phoca hispida*) and walrus (*Odobenus rosmarus*) blubber in the Canadian Arctic, in concentrations ranging from 0.095 to 0.626 mg kg^{-1} wet weight (Tomy *et al.,* 1998b; 2000). It was observed in this study that the concentration profiles for the Arctic marine mammals show a predominance of the shorter carbon chain length congeners (the C_{10} and C_{11} groups). SCCPs have also been measured in the liver and muscle of seabirds from the European Arctic in concentrations ranging from 0.005 to 0.088 mg kg^{-1} wet weight (Reth *et al.,* 2006).

For the terrestrial environment, the data is very limited. CEFAS (1999) reported the concentrations of

SCCPs in earthworms from the UK ranging from <0.1 to 0.7 mg kg^{-1} dry weight. Campbell and McConnell (1980) determined levels of $C_{10–20}$ CPs in birds (100-1200 µg kg^{-1} wet weight) and seabird eggs (non-detect to 2000 µg kg^{-1}) from the UK.

Concentrations in human tissues are very limited. A study from the United Kingdom has found SCCPs to be present in human breast milk at concentrations ranging from 49 and 820 ng g^{-1} fat (median 180 ng g^{-1} fat) (Thomas *et al.*, 2006). Tomy (1997) measured SCCPs in human breast milk from Inuit women in Canada at a concentration of 11–17 µg kg^{-1} lipid (mean 13 µg kg^{-1} lipid). The only market basket study which was conducted for SCCPs estimated the 95th percentile of the total daily intake for 1-year-old Japanese female to be 6.8×10^2 ng kg^{-1} day and concluded that food intake is the main exposure pathway of SCCPs for Japanese people, but it does not pose a risk (Iono *et al.*, 2005).

It is thought that the main route of exposure to SCCPs is likely to be dermal, however inhalation and food may be important routes of uptake, because of their high Kow. SCCPs were the second most abundant group of compounds measured in indoor air of homes in France, with a mean concentration of 45 µg g^{-1} dust (Bonvallot *et al.,* 2010). In the only survey of foodstuffs from the litareture, the highest concentration of chlorinated paraffins (average level of C_{10-20}: 300 µg kg^{-1}) was present in dairy products (Campbell and McConnell, 1980). If we assume a daily consumption of dairy products of 1 kg per person, the daily intake of SCCPs and MCCPs would be 300 µg (4.3 µg kg^{-1} body weight, assuming an average body weight of 70 kg).

3. EFFECTS AND TOXICITY

Early dietary exposure studies of juvenile rainbow trout (*Oncorhynchus mykiss*) with SCCPs showed rapid accumulation and high assimilation efficiencies from food (Fisk *et al.*, 1998). Half-lives of SCCPs in rainbow trout ranged from 7 to 53 days and increased with increasing carbon chain length, chlorine content and Kow. SCCPs have been shown to decrease free and total plasma T4 concentrations, and double plasma TSH levels (Wyatt *et al.*, 1993). Compared to MCCPs, SCCPs are more potent as peroxisome proliferators and may lead to thyroid follicular cell carcinogenesis, as observed in long-term studies with rats and mice (Wyatt *et al.*, 1993). The International Agency for Research on Cancer (IARC) has concluded that there is sufficient evidence for the carcinogenicity of a commercial chlorinated paraffin product of average carbon chain length C_{12} and average degree of chlorination of 60% in experimental animals and “possibly carcinogenic to humans” (Group 2B) (IARC, 1990).

Experiments with freshwater and marine algae exposed to SCCPs ($C_{10–12}$, 58% Cl) revealed a higher sensitivity of marine algae compared to freshwater algae, with an EC_{50} of 43 mg L^{-1}, compared to 1,310 mg L^{-1} (Thompson and Madeley, 1983a; 1983b).

The effects of SCCPs on the survival and reproduction of five soil organisms (*Fosomia candida, Eisenia fetida, Enchytraeus albidus, Enchytraeus crypticus,* and *Caenorhabditis elegans*) were investigated by Bezchlebová *et al*. (2007). *Folsomia candida* (collembola) was most sensitive organism, with an LC_{50} for adult survival of 5733 mg kg^{-1} dry weight and EC_{50} and EC_{10} values for reproduction of 1230 and 660 mg kg^{-1} dry weight, respectively.

In a long-term study with laying hens, SCCPs were found in the highest concentrations in abdominal fat, in the yolk and the liver, in relation to the amounts ingested (Ueberschär *et al.*, 2007). Half-lives ranged from 20-30 days for most tissues, and the input-output balance revealed the highest extraction amount (30%) through manure and urine. In birds, both acute and chronic toxicity of SCCPs appears to be low. In a reproductive study with mallard ducks (*Anas platyrynchos*) fed with a diet of a $C_{10–13}$ SCCP, a slight decrease in eggshell thickness and 14-day embryo viability were observed only at the highest dose (Serrone *et al*., 1987).

SCCPs do not seem to cause mutagenic effects in bacterial assays *in vitro*, or in rats (NTP, 1986; IRDC, 1983). In mammalian cells, the SSCP C_{12}; 60% Cl has been found to be mutagenic in mouse lymphoma cells (Myhr *et al*., 1990). Another in vitro study has shown that SCCPs may act as tumour promoters (Kato and Kenne, 1996). Limited data is available on neurotoxicity. A study with male

mice observed a decreased motor capacity, after administration of male mice with a dose of 300 mg kg^{-1} bw of SCCP ($C_{10–13}$, 49% Cl) (Eriksson and Kihlström (1985).

4. CONCLUDING REMARKS

It is clear that sensitive analytical methods need to be established, in order to improve future monitoring efforts. Further research is needed in order to understand the mechanisms of toxicity of SCCPs. The neurotoxicity data is limited and the immunotoxicity data is non-existent. Despite some sporadic efforts to determine the influence of chain length and degree of chlorination, more information is needed on the dynamics, kinetics and metabolism of SCCPs. Toxicity studies in rodents and other animals indicate that chronic exposure to relatively low concentrations of SCCPs adversely affects their survival and development. Finally, more human biomonitoring data is needed, in order to understand the routes of uptake of these chemicals in the human body and the levels present in tissues.

It is evident that SCCPs may lead to adverse environmental and human health effects. Given their persistence, bioaccumulative nature and potential to undergo long-range transport, it is clear that action is required for the regulation of these chemicals.

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