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Consideration of chemicals newly proposed for inclusion in Annexes A, B or C of the Convention: Short-chained chlorinated paraffins

Summary of short-chained chlorinated paraffins proposal

Note by the Secretariat

1. The annex to the present note provides a summary prepared by the Secretariat of the proposal submitted by the European Union and its member States that are Party to the Stockholm Convention on Persistent Organic Pollutants for listing short-chained chlorinated paraffins in Annexes A, B or C of the Stockholm Convention pursuant to paragraph 1 of Article 8 of the Convention. The complete proposal is contained in document UNEP/POPS/POPRC.2/INF/6.

Possible action by the Committee

2. The Committee may wish:

(a) To consider the information provided in the present note and in document UNEP/POPS/POPRC.2/INF/6;

(b) To decide whether it is satisfied that the proposal fulfils the requirements of Article 8 and Annex D of the Convention;

(c) To develop and agree on, if it decides that the proposal fulfils the requirements referred to in subparagraph (b) above, a work plan for preparing a draft risk profile pursuant to paragraph 6 of Article 8.

* UNEP/POPS/POPRC.2/1.

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Annex

Proposal for listing short-chained chlorinated paraffins (SCCPs) in Annexes A, B or C of the Stockholm Convention on Persistent Organic Pollutants

Introduction

1. Short-chained chlorinated paraffins (SCCPs) are a group of synthetic compounds mainly used in metal working fluids, sealants, as flame retardants in rubbers and textiles, in leather processing and in paints and coatings.

2. The available data from remote areas clearly show contamination of biota and air by SCCPs. SCCPs are highly toxic to aquatic organisms. They do not break down naturally and tend to accumulate in biota. Their persistence, bioaccumulation, potential for long-range environmental transport and toxicity mean that they may have damaging environmental effects at a global level.

3. This dossier focuses solely on the information required under paragraphs 1 and 2 of Annex D of the Stockholm Convention and it is mainly based on:

(a) European Commission (2000). European Union Risk Assessment Report, Vol. 4: alkanes, C10-13, chloro-. European Chemicals Bureau, Brussels, Belgium. 166 pp. (EUR 19010; ISBN 92-828-8451-1). http://ecb.jrc.it/existing-chemicals/;

(b) European Commission (2005), Final Draft. Updated Risk Assessment of Alkanes, C10–13, Chloro-, Combined draft of August 2005. http://ecb.jrc.it/existing-chemicals/.

(c) Filyk, G, Lander, L, Eggleton, M, Muir, D, Puckett, K. (2003) Short Chain Chlorinated. Paraffins (SCCP) Substance-Final Draft II. Environment Canada. Dossier prepared for UNECE ad hoc Expert Group on POPs. http://www.unece.org/env/popsxg;

(d) WHO (1996). Chlorinated Paraffins, Environmental Health Criteria Report No 181. World Health Organization, Geneva, http://ecb.jrc.it/existing-chemicals/.

4. These reviews and other references (as provided in document UNEP/POPS/POPRC.2/INF/6) serve as a source of further information referred to in paragraph 3 of Annex D of the Stockholm Convention on this candidate POP chemical.

1 Identification of the chemical

5. SCCPs are n-paraffins that have carbon chain lengths of between 10 and 13 carbon atoms and a degree of chlorination of more than 48% by weight. There is a range of commercially available C10-13 chlorinated paraffins and they 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.

6. Two other groups of chlorinated paraffins are made commercially. These are known as "mid, medium or intermediate chain length" (typically C14-17) and "long chain length" (typically C20-30). This dossier, however, concerns only the short chain length (C10-13) chlorinated paraffins.

1.1 Names and registry numbers

IUPAC[1] Name: Alkanes, C_{10-13}, chloro

Synonyms: alkanes, chlorinated;
alkanes (C_{10-13}), chloro-(50-70%);
alkanes (C_{10-13}), chloro-(60%);
chlorinated alkanes;
chlorinated paraffins;
chloroalkanes;

1 International Union of Pure and Applied Chemistry.

chlorocarbons;
polychlorinated alkanes;
paraffins chlorinated.

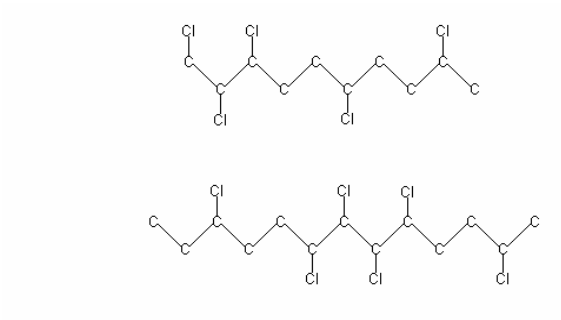
CAS[2] No: 85535-84-8

EINECS[3] No: 287-476-5

1.2 Structure

Molecular formula: $C_xH_{(2x-y+2)}Cl_y$, where x = 10-13 and y = 1-13

The structure of two example SCCP compounds ($C_{10}H_{17}Cl_5$ and $C_{13}H_{22}Cl_6$) is shown below.



Molecular weight: 320-500

2 Persistence

7. Atmospheric half-lives of 1.9-7.2 days have been estimated for SCCPs (European Commission, 2000). Nevertheless, in the aqueous phase, rates of hydrolysis, photolysis with visible or near UV radiation, oxidation and volatilization are insignificant under ambient temperatures (Government of Canada, 1993). Photolytical degradation in aqueous media may take place, but at a very slow rate (Koh and Thiemann, 2001; El-Morsi et al. 2002)

8. SCCPs are not readily or inherently biodegradable in standard tests. It can be concluded from the simulation tests that SCCPs with low chlorine content (e.g. <50% wt Cl) may biodegrade slowly in the environment in the presence of adapted microorganisms. An additional simulation study on degradation of SCCPs in the marine environment has been required recently within the EU and the results of the study should be available by the end of 2006.

9. In its opinion given in 2003 (CSTEE 2003), the EU Scientific Committee on Toxicity, Ecotoxicity and the Environment came to the conclusion that SCCPs are potentially persistent (P) and possibly very persistent (vP). The Committee emphasised the evidence that SCCPs are occurring in remote areas and were of the view that this is particularly important evidence that gives further support to the P/vP classification. Weight of evidence indicates that the half-life of SCCPs in sediment is greater than 1 year

10. The available information seems to indicate that SCCPs have long half-lives in the environment.

3 Bioaccumulation

11. Reported log Kow of different SCCPs range from 4.39 to 8.69, indicating a high potential for bioaccumulation (European Commission, 2000).

12. High bioconcentration factors (BCFs) in fish have been reported in the scientific literature (European Commission, 2000). In one of the key studies, whole body BCFs of 1 173-7 816 were determined based on radioactivity measurements in the fish and BCFs of 574-7 273 were determined based on the parent compound analysis (Madeley and Maddock 1983).

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2 Chemical Abstracts Service.

3 European Inventory of Existing Chemical Substances.

13. In addition to these experimental values from laboratory studies, BCF values have been estimated *in situ* for Lake Trout (*Salvelinus namaycush*) in western Lake Ontario, i.e., the overall BCF for C10-13 SCCPs was 36 500 (Filyk et al. 2003). Bioconcentration in mussels has also been assessed with reported whole body BCFs ranging from 5 785 to 40 900 (European Commission 2000).

14. SCCP have high reported values of both log Kow and BCF for different aquatic species.

4. Potential for long-range environmental transport

15. Drouillard et al. (1998a) have determined vapour pressures for a range of SCCPs. In the EU Risk Assessment Report (European Commission, 2000), an assumed vapour pressure of an SCCP with chlorine content of approximately 50% of 0.0213 Pa at 40°C is used. Henry's Law constants range from 0.7 to 18 Pa m3/mol, near the values of some acknowledged POPs (Drouillard et al. 1998a). This constant and vapour pressure are the most important chemical characteristic to determine whether a substance may undergo long-range environmental transport in the atmosphere. As shown in table 1, Henry's Law constants are in the range of those for currently listed POPs. Therefore, based on their chemical properties, SCCPs are likely to undergo long-range environmental transport in the atmosphere. Moreover, atmospheric half-lives exceeding the screening criteria of 2 days (1.9-7.2 days) have been estimated for SCCPs (European Commission, 2000).

Table 1: Water solubility (WS), vapour pressure (VP) and Henry's Law Constant (HLC) (at 25 °C) for SCCPs and currently listed POPs

Substance	WS mg/L	VP Pa	HLC Pa m^3/mol
SCCP-min	0.0224**	2.8×10^{-7} *	0.7 *
SCCP-max	0.994**	2.5 *	18 *
POP-min	0.0012 (DDT)	2.5×10^{-5} (DDT)	0.04 (endrin)
POP-max	3.0 (toxaphene)	27 (toxaphene)	3726 (toxaphene)
POP-2nd max	0.5 (dieldrin)	0.04 (heptachlor)	267 (heptachlor)

* Drouillard et al. 1998a
** Drouillard et al. 1998b

16. SCCPs have been found in air samples from a remote area in the Canadian Arctic (Peters et al., 1998). The mean total concentrations (vapour + particulate phase) found were 20 ±32 pg/m3 at the remote site. Tomy (1997a; as reported in Tomy, 1998) found that SCCPs were present in air from Egbert, Canada, at a concentration of 65-924 pg/m3. Muir et al. (2001) reported SCCPs to be present at a concentration of 249 pg/m3 in air overlying the west basin of Lake Ontario. The levels of SCCPs in air from the Arctic have also been reported by Bidleman et al. (2001). The levels found ranged from 1.07 to 7.25 pg/m3 and were dominated by the contributions from chlorodecanes (C10 fractions).

17. The concentrations of SCCPs (vapour + particulate phase) reported in the Arctic environment ranged from 1.07 to 7.25 pg/m3 (Borgen et al., 2000) and from 1.8 to 10.6 ng/m3 (Bidleman et al., 2001). Tomy et al. (1997 and 1999) reported SCCPs in surface sediments from the Canadian mid-latitude and Arctic regions, and attributed these to long-range transport. Stern (2003, as reported in Filyk, 2003) found levels of SCCPs in a lake sediment core taken from a very remote lake in Arctic Canada (75o34'N; 89°19'W) which provides evidence for transport to, and deposition in, the Arctic (Filyk et al. 2003).

18. SCCPs have been reported in marine mammals from various regions of the Arctic (Stern et al., 1997; Tomy et al., 1998). There is also evidence of SCCP accumulation in fish species from Lake Ontario (Muir et al., 2001).

19. The study of Stern et al. (1997) also detected SCCPs in three samples of breast milk taken from Inuit women living in settlements along the Hudson Strait of Canada. A study performed by Thomas et al. (2006) found similar SCCP concentrations in breast milk of women from the United Kingdom.

20. The ubiquity of SCCPs, the vapour pressures reported, and the Henry's Law Constant values (similar to those of acknowledged POPs), indicate that SCCPs are transported long range.

5 Adverse effects

21. According to EU Risk Assessment Report (European Commission, 2000) SCCPs are of low acute toxicity to fish, with 48 and 96-hour LC50 values in excess of the water solubility of the substance. Chronic toxicity values include a 60-day LC50 of 0.34 mg/L for rainbow trout and no observed effect concentrations of <0.040 and 0.28 mg/L for rainbow trout and sheepshead minnows respectively.

22. For aquatic invertebrates, SCCPs are of high toxicity with 24-hour EC50 values with daphnids ranging from 0.3 to 11.1 mg/L and with acute NOECs ranging from 0.06 to 2 mg/L. In 21-day tests with daphnids, EC50 values ranged from 0.101 to 0.228 mg/L and NOECs ranged from 0.005-0.05 mg/L. For algae, 96-hour EC50 values ranged from 0.012 to 3.7 mg/L, depending on the species.

23. Information available from acute studies and skin irritation studies in animals indicates that the intensity and nature of effects for these endpoints are independent of chain length and degree of chlorination. Assessment of the available data clearly indicates that SCCPs are of low acute toxicity in animals. In rodent carcinogenicity studies, dose-related increases in the incidence of adenomas and carcinomas were observed in the liver, thyroid and kidney. Other cancers seen were dismissed as not significant. Consideration of the likely underlying mechanisms for these tumours suggests that they are not relevant to human health.

24. There are no data available on the effects of SCCPs on fertility in humans or animals. An SCCP produced developmental effects in rats at a dose which also caused maternal toxicity (2 000 mg/kg body weight). No developmental effects were observed in a study in rabbits, although maternally toxic doses were not tested. NOAELs for general toxicity of 100 and 1 000 mg/kg/day were identified in rats and mice respectively.

25. The relevance of the finding that medium-chain length chlorinated paraffins can cause a severe effect (internal haemorrhaging leading to deaths) in suckling rat pups has been recently discussed (European Commission, 2005).

26. The current EU hazard classification for SCCPs is: Carc. Cat. 3; R40 - N; R50-53 (Risk Phrases: R40: Limited evidence of a carcinogenic effect; R50/53: Very toxic to aquatic organisms; may cause long-term adverse effects in the aquatic environment.). Also the International Agency for Research on Cancer (IARC) has designated SCCPs (as a group) as possible carcinogens.

27. In summary, SCCPs are of high aquatic toxicity to a variety of species, and its terrestrial toxicity may be an additional cause of concern. SCCPs are also possible carcinogens.

6 Statement of the reasons for concern

28. The proposal of the European Union and its member States contains the following Statement of Concern:

> “SCCPs are highly toxic to aquatic organisms and it is considered as a possible carcinogen. SCCPs do not break down naturally and tend to accumulate to biota. The available data from remote areas clearly show contamination of the environment and biota by SCCPs. Their persistence, bioaccumulation and toxicity mean that they may have damaging environmental effects at a global level. Overall, it can be considered that SCCPs meet the screening criteria for persistence, potential to cause adverse effects, bioaccumulation and potential for long range environmental transport.
>
> Placing on the market and use of SCCPs have been restricted over the last years in the European Union but no total prohibition has yet been foreseen. On the other hand, production and use of SCCPs continues unrestricted in many other countries. As SCCPs can move in the atmosphere far from [their] sources, single countries or groups of countries alone cannot abate the pollution caused by [them]. Due to the harmful POP properties and risks related to its widespread production and use, international action is warranted to control this pollution.”