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SCIENTIFIC COMMITTEE ON TOXICITY, ECOTOXICITY AND THE ENVIRONMENT (CSTEE)

OPINION OF THE CSTEE ON "Short-Chain Chlorinated Paraffins (SCCPs)" Follow-up of Directive 2002/45/EC

Opinion expressed at the 35th CSTEE plenary meeting

Brussels, 17 December 2002

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TERMS OF REFERENCE

Directive 2002/45/EC restricts the use of SCCPs, especially in metal working fluids and leather finishing products. According to Article 1 of this Directive, the Commission is now reviewing all remaining uses of SCCPs in the light of any relevant new scientific data on risks posed by these substances to health and the environment, in cooperation with Member States and the OSPAR Commission.

The Commission has therefore asked the CSTEE the following question:

> Is the CSTEE aware of any new available scientific evidence concerning SCCPs which could influence the results of the risk assessment and might call for a modification of its conclusion?

BACKGROUND

Chlorinated paraffins (CPs) are very complex mixtures, and are often divided into several groups depending on the chain length of the starting material and the amount of chlorine in the final product. Three major groups are short, medium and long chained chlorinated paraffins (SCCPs, MCCPs and LCCPs, respectively), but it has to be realised that there are several types of products covered by these acronyms, and there are at least twenty different CAS numbers registered for CPs.

SCCPs were on the first priority list for risk assessment of existing chemicals under the Council regulation (EEC) 793/93, and CSTEE has, at its meeting of 27 November 1998, expressed an opinion on the Final Draft of the Risk Assessment Report for this group.

The restrictions introduced by Directive 2002/45/EC were directed towards the use in metal working fluids and leather finishing products, the two areas identified in the RAR as being responsible for unacceptable sources for emissions to the aquatic environment. The major use of SCCPs has been in metal working fluids, and the restrictions will probably decrease the environmental and occupational exposure considerably.

CSTEE COMMENTS

New assessments

Several new assessments of SCCPs have been done since the EU RAR was published. UN ECE is investigating several chemicals that may be added to their LRTAP Convention for POPs, and SCCPs is one of these groups (UN ECE, 2002). OSPAR has been interested for a long time in SCCPs and has a background document on this group of substances (OSPAR, 2001), and HELCOM has also recently published a guidance document on SCCPs (HELCOM, 2002). Australia has produced an assessment of SCCPs (NICNAS, 2001). A review article has also been published by Tomy *et al.* (1998), as well as a monograph called "Toxicological risks of selected flame-retardant chemicals" (National Research Council, 2000) containing a chapter on CPs. Using these documents and some material found in a limited literature search, the CSTEE has tried to get an updated picture of the knowledge on SCCPs.

Use

The amount of SCCPs used in EU Member States seems to have been significantly reduced during the 1990s (OSPAR, 2001). The CSTEE would, however, like to draw attention to the fact that future restriction on the use of brominated flame retardants may increase the use of CPs for this purpose. There is also information indicating that large volumes are being produced in China and there is thus a risk for considerable import in goods.

In addition to the present restricted uses, SCCPs have been used as plasticizers in polymers, especially PVC. Both mats, for floor and wall cover, and PVC covered wall papers can contain SCCPs, which may be sources of human exposure indoors, but there are no published studies known to the CSTEE. A recent experiment also showed that the cleaning water used on a SCCP containing mat contained this chemical (B. Jansson, personal communication), which also indicates the possibility of environmental exposure.

Among other building material that may contain SCCPs are fillers and sealants. Before PCB was banned, it was used in high concentrations in sealants, and SCCPs were one of the substitutes, when PCB was phased out. No report on emission of SCCPs from such materials is known, but they can be expected to behave like PCB, which has been reported to be distributed to both indoor and outdoor environments (Johansson *et al.,* 2001).

Properties

Muir et al. (2000) have performed homologue specific analyses of SCCPs in both water and lake trout in Lake Ontario. It is thus possible to calculate bioaccumulation factors for these groups and they found 21000 (C_{10}), 38000 (C_{11}), 34000 (C_{12}) and 114000 (C_{13}). It is not possible to see what bioaccumulation value the assessors used in the EU risk assessment, but these high BAF values may have implications for the conclusions.

Exposure data

There are some new studies on levels of SCCPs in the environment. There are still considerable analytical difficulties, as there are so many compounds in the products. It is impossible to analyse individual congeners, and the results have, in most cases, been related to the technical products. In the environment, however, there is a mixture of products with different chain lengths and chlorination degrees, which further complicate the determinations. In the draft risk assessment report on medium chain chlorinated paraffins (Environment Agency, 2002) several of the referenced studies give results for the sum of short and medium chain CPs. A Canadian research group has developed a technique using HRGC-HRMS (Tomy *et al.,* 1997a), which is better than other described methods, but rather expensive and we cannot hope to see a lot of results produced with it. This lack of useful methods to determine the CPs is a drawback, as it is difficult to see if the present restrictions will influence the environmental conditions. The development of methods for the determination of prioritised substances in the Water Framework Directive, in which SCCPs are included, may improve this situation.

Air concentrations of SCCPs have been measured far away from known sources, indicating that these substances are effectively transported over long distances. Thus Tomy *et al.* (1998) measured <1 – 8.5 pg/m^3 in northern Canada and Borgen et al. (2000) 9.0 – 57 pg/m3 at Svalbard. In Egbert, Ontario, Tomy *et al.* (1998) measured 65 – 924 pg/m^3, while Peters *et al.* (2000) found 320 pg/m^3 (arithmetic mean) in Lancaster, UK. In the latter study it was found that about 95% of the SCCPs were present in the gas phase. High concentrations, between 1.8 and 10.6 ng/m^3, have been measured at Bear Island (Borgen *et al.*, 2002).

Wastewater from Canada has also been analysed for SCCPs and levels between 59 and 448 ng/L were found (Muir *et al.* 2000). In the same investigation water from Lake Ontario was found to contain up to 1.8 ng SCCPs/L. In harbour sediments from the same lake, concentrations of SCCPs ranged from 5.9 to 290 ng/g dry weight. Tomy *et al.* (1997b) studied sediment from an arctic lake in Canada where 7 ng/g dry weight was measured. SCCPs have also been found to be rather evenly distributed in sediments from Lake Ontario, with an average concentration of 36 ng/g, which is similar to that of TotalDDTs 32 ng/g (*Marvin et al.*, 2002).

Trout, char and burbot from Norway have been analysed for SCCPs (Schlabach *et al.* 2001). The concentrations (in ng CPs/g fresh weight) found were 3.1 – 3.6 in trout, 6.9 in char and 38 – 608 in burbot. Carp and lake trout from Lake Ontario have been shown to contain from 59 to 2600 ng SCCPs/g wet weight whole fish (Muir *et al.* 2000). Rainbow trout and carp samples from western Lake Ontario have also been analysed for SCCPs and MCCPs by Bennie *et al.* (2000). They report the sum of the two CPs (SMCCPs) and found mean concentrations of 0.90 microgram/g wet weight in carp and 2.7 microgram/g wet weight in rainbow trout. Tomy *et al.* (1997) analysed yellow perch and catfish from Detroit River and found 1100 and 300 ng SCCPs /g wet weight, respectively. Marine mammals also contain SCCPs, as shown by Stern *et al.* (1998) and Tomy *et al.* (2000), and concentrations measured in blubber from beluga whales and walrus were from 110 to 1360 ng/g wet weight. Bennie *et al.* (2000) have analysed SMCCPs in beluga whales from the St. Lawrence River estuary. The liver contained 1.1 – 59 and the blubber 6.4 – 166 microgram SMCCPs/g fresh weight. The beluga blubber levels are comparable to total concentrations of PCB and DDT compounds.

SCCPs plus MCCPs in several environmental compartments in the UK have been determined by Nicholls *et al.* (2001). They sampled from 20 aquatic and 6 terrestrial sites and found the following ranges of CPs: sediment <0.2-65.1 mg/kg dry weight, water <0.1-1.7 microgram/L, fish <0.1-5.2 mg/kg wet weight, benthos < 0.05-0.8 mg/kg wet weight, digested sewage 1.8-93.1 mg/kg dry weight, soil <0.1 mg/kg dry weight, and earthworms <0.1-1.7 mg/kg wet weight. It is clear from this study that CPs are widely distributed in the UK environment.

Fate

^{14}C labelled CPs with a chain length of twelve carbons have been shown to be readily bioavailable to sediment-ingesting oligochaetes (Fisk *et al.*, 1998a). A strain of the genus *Rhodococcus* isolated from an environmental water sample have been shown to degrade SCCPs (Allpress and Gowland, 1999).

Juvenile rainbow trout were given a diet containing CPs with chain lengths C_{10}, C_{11}, and C_{14} with different chlorination degrees (Fisk et al., 1998b). All CPs were rapidly accumulated from the food and had high assimilation efficiencies. Half lifes of the CPs ranged from 7 to 53 days, and were positively correlated with K_{ow}, chain length and chlorine content.

Effects

Cooley *et al.* (2001) were dosing CPs of specific chain lengths to juvenile rainbow trout for 21 days to study effect on behaviour and liver, and for 85 days to assess histology for longer term exposure. Many of the trout (whole fish concentrations of 0.22 – 5.5 microgram/g) showed diminished or no startle response, loss of equilibrium, and developed dark coloration. These responses are indicative of a narcotic toxicological mode-of-action. Histopathological lesions were observed in livers for all dose groups.

The acute toxicity of "synthetic" CPs with different chain lengths have been studied in Japanese medaka (*Oryzias latipes*) eggs (Fisk *et al.*, 1999). Compounds with ten carbon atoms were found to be more toxic than C_{11}, C_{12}, and C_{14}. The results indicate that the acute toxic mechanism is narcosis. For C_{10} compounds no significant difference could be seen for different chlorination degrees.

In vitro percutaneous absorption experiments have been conducted with human skin sections (Roy *et al.*, 1998). Using the default values recommended by US EPA, they gave a dermally absorbed dose value of 0.037 mg/kg/day. The low dose linear extrapolation model based on earlier NTP two-year oral feeding studies gave a cancer risk of approximately 1 in 20,000.

The effect of CPs and several other persistent organic compounds on thyroid hormone levels have been investigated in rats (Hallgren and Darnerud, 2002). Combination effects between CPs and a brominated diphenyl ether on T4 and EROD induction levels were indicated in these experiments.

Conclusions

The knowledge on SCCPs has increased since the RAR was published, especially on their presence in the environment. It is obvious that these compounds can be transported over long distances and that they can be bioaccumulated. There is still a lack of information on levels in humans, and the data on effects are still rather scarce.

The information on sources is limited, but it is believed that the use in metal working fluids has been a major source. The emissions from other applications are more difficult to judge at present, but an increased use of SCCPs as a flame retardant may increase the importance of those in the future. Direct exposure from articles containing these substances needs further studies.

CSTEE is not of the opinion that the new scientific data change the conclusions drawn in the RAR.

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