CHLORINATED PARAFFINS - A FURTHER POP TO CONSIDER?

Heinz-Jochen Poremski[1], Suzanne Wiandt[1], Thomas Knacker[2]

[1] Umweltbundesamt (Federal Environmental Agency), Bismarckplatz 1, D - 14193 Berlin, Germany ; [2] ECT Oekotoxikologie GmbH, Böttgerstr. 2 – 14, D – 65439 Flörsheim a.M.

Introduction

Chlorinated Paraffins (CPs) are qualified as substances which serve as additives in metal working fluids, leather industry, flame retardants and plasticisers in paints, sealants and polymers such as PVC and rubbers and even as solvents in carbonless copy paper. Most of these applications have an open access and release to man and the environment. Furthermore, their inherent properties are of high concern for the environment as they indicate strongly to be persistent, liable to bioaccumulate and toxic (i.e. PBT-substances).

The physico-chemical properties allow a widespread distribution once they enter the environment and by that CPs may also reach remote areas far form the source of emissions and may undergo enrichment in the food chain and bioaccumulation in organisms.

Risk assessment and risk management showed a need for regulating the Short Chained Chlorinated Paraffins (SCCPs) and restrict their use in main fields of current applications. OSPAR and the EU–Programme on Existing Chemicals suggested these measures and legislation is currently drafted by the EU-Commission. However, it remains unresolved whether medium (MCCPs) and long (LCCPs) chained chlorinated paraffins should be dealt within a grouping approach. The following paper discusses a grouping approach comparing properties and use patterns. Special importance is given to the occurrence in remote areas.

Use

SCCPs are mainly used as extreme pressure additives in metal working fluids. Further they are used as flame retardants and plasticisers in rubbers, paints and other polymeric materials and as additives to adhesive and sealants. Minor amounts are used in leather processing and even smaller amounts as secondary plasticisers in polyvinyl chloride (PVC)[1].

MCCPs are mainly used as secondary PVC plasticisers. Further uses are as extreme pressure additives in metal working fluids, as plasticisers in paints, as additives to adhesive and sealants, in fat liquors used in leather processing, as flame retardants and plasticisers in rubbers and other polymeric materials, and as solvent in carbonless copy paper[2].

LCCPs can be divided into three subclasses ($C_{18\text{-}20\ liquids}$, $C_{>20\ liquids}$, and $C_{>20\ solid\ waxes}$). The main use of $C_{18\text{-}20\ liquids}$ is in additives for paints, the $C_{>20\ liquids}$ are used essentially as flame retardants for rubber and textiles, and the $C_{>20\ solid\ waxes}$ are also used mainly in paints. Altogether, the main use of LCCPs is as flame retardants for rubber and textiles.

Release to the environment

The release of CPs to the environment could occur during production, storage, transportation, industrial use, disposal and burning of waste and landfilling of products such as PVC, textiles, painted materials, paint cans and oils containing chlorinated carbons[3].

The uses of chlorinated paraffins probably provide the major source of environmental contamination. For example, CPs effectively dissolved in polymers will leak into the environment very slowly, but might act as sources of chlorinated paraffins for centuries after disposal[4].

LCCPs might only be emitted into the environment when used as metal working lubricants and leather fat liquor[1]. However, MCCPs can be released to the environment when used as secondary PVC plasticisers, as plasticisers in paints, as additives to adhesive and sealants, as flame retardants and plasticisers in rubbers and other polymeric materials[2,5]. Since the physico-chemical properties of MCCPs and LCCPs overlap to a large degree, the emission of LCCPs into the environment for all applications cannot be excluded. Taking into account the gradual shift of physico-chemical properties from SCCPs to LCCPs, which indicate decreasing mobility of CPs in the environment with increasing carbon chain length, and taking into account the stability of all CPs under environmental conditions, one might expect a delayed release of LCCPs compared to MCCPs and SCCPs.

Physico-Chemical Properties

Physico-chemical properties of CPs are dominated by two factors: the carbon chain length and the degree of chlorination. SCCPs, MCCPs and LCCPs consist of a large amount of different chemicals which as a result are denoted not by a single value but by a range for each of the physico-chemical properties. These ranges of values partly overlap for SCCPs, MCCPs and LCCPs. When assuming that all three fractions of CPs belong to one group of substances, the range between the highest and lowest value for the respective physico-chemical property is larger than for a single fraction. However, the separation of the different fractions based on carbon chain length seems to be arbitrary when taking into account the physico-chemical properties.

Biodegradation

In standardised biodegradation tests it has been clearly shown that SCCPs are not biodegradable. For MCCPs and LCCPs standardised test data are not available. There are only very few indications that CPs may degrade slowly in acclimated or cometabolic systems. Anaerobic conditions might allow some degradation for LCCPs. Overall, SCCPs, MCCPs and LCCPs are considered to be neither abiotically nor biotically degradable in the aqueous medium.

Bioaccumulation

Bioconcentration in marine mussels is 10 to 100fold higher than in fish. In both organisms bioconcentration decreases with increasing carbon chain length, while depuration half-life seems to increase with increasing carbon chain length. Bioaccumulation via food in fish and the measured exposure levels in birds, top predators and human foodstuff demonstrate that CPs are taken up via the food chain.

Effects

The long-term ecotoxicological effects of chlorinated paraffins to aquatic organisms are strongest when exposed to daphnids. Further it seems that the long-term effect threshold of SCCPs, MCCPs

and LCCPs to daphnids is very similar while for fish and algae the toxicity is less pronounced and seems to decrease with increasing carbon chain length.

Environmental Levels: Remote Areas, Air and biota

It was investigated whether SCCPs were being transported to the Arctic, and if so, whether they accumulated in marine mammals and ultimately, in the Northern people who consume these animals as part of their traditional diet. In the marine mammal blubber derived from Ringseal, Beluga and Walrus from various regions in the Arctic between 199 and 526 μg/kg wet weight were found compared to 785 μg/kg wet weight found in blubber from Beluga sampled from the St. Lawrence River estuary. In human breast milk collected from women living in the settlements along the Hudson Strait between 10.6 and 16.5 ng/g (lipid weight) were measured. The authors concluded that SCCPs are atmospherically transported to the Arctic and bioaccumulate in both marine mammals and in the Northern people who consume them.[6]

CPs were detected in water samples collected at the Bermuda Islands. The distribution of CPs through the water column down to a depth of 1,200m was investigated: 50 μg/L in the surface film, at depths of 15, 250, 900 and 1,200 m the concentrations were near the detection limit of 3 ng/L; at the depth of 350 m a concentration of 0.02 μg/L was measured. In water from the Maledives CPs were not found. Both sites, Bermuda Islands and Maledives, are considered to be remote from industry. It was explained that the occurrence of CPs at the Bermuda Islands is resulting mainly from atmospheric transport and partly from transport by currents.[7]

All fractions of chlorinated paraffins at levels of low ng values, in particular medium- and long-chained CPs, were detected in the deep sea fish *Sebastolobus altivelis*. However, the small amount of sample did not allow to exactly quantify the CPs in the fish tissue.[8]

Recent data on the levels of SCCP and MCCP in beluga whale (*Delphinapterus leucas*), rainbow trout (*Oncorhynchus mykiss*) and carp (*Cyprinus carpio*) from Canada have been reported[9]. For the whale, the samples were taken from dead animals from the St. Lawrence River between 1987 and 1991. It is concluded in this study that the beluga whales have elevated levels of SMCCPs in their blubber and liver tissue and these data are comparable to PCB and DDT levels found in the same species. The beluga whale data reported are much higher than for other marine mammal data for CPs. Despite the problems encountered in the analytical determinations of the different CP fractions, it seems that the levels found of SCCPs and MCCPs are quite similar. Referring to the lower BCF value found for one MCCP compound, it can be again argued that the biomagnification potential for MCCPs is quite higher than expected from the BCF value determined experimentally. It has to be noted though that most of the available data on long range transport are mainly data for SCCPs or have not been further specified in the literature.

Conclusion

Intensive data collection and comparison of data on all three fractions of chlorinated paraffins has been carried out. It is concluded that CPs should be considered as a group of similar substances which mainly differ by chain length and degree of chlorination but show similar partitioning, degradation and accumulation behaviour in the environment. Moreover it is concluded that CPs can be considered as PBT substances (table 1).

Table 1: Persistence, bioaccumulation and toxicity of CPs.

	SCCP	MCCP	LCCP
Persistence	not degradable	not degradable	not degradable
Bioaccumulation	log Ko/w: 4.4-8.7 .BCF: 24,800-40,900*	log Ko/w: 5.5-9.0 BCF: 2,100-2,900*	log Ko/w: 7.9-12.7 BCF: 200-1,200*
Toxicity (long-term NOEC)	5-50 μg/L	1.6-4 μg/L	LOEC: <1.2 μg/L

* BCF in marine mussels

POP criteria have been developed within the POP Convention[10], covering persistence (e.g. half life of 2 months in water), bioaccumulation (e.g. BCF in aquatic species greater than 5,000 or, in the absence of such data, log Ko/w greater than 5), adverse effects (e.g. evidence of adverse effects to human health or to the environment) and the potential for long-range environmental transport (e.g. measured levels of the chemical in locations distant from the sources of its release that are of potential concern). Long range transport for CPs can be assumed due to monitoring data in remote areas, especially for SCCPs. The PBT character clearly indicate that CPs can be considered as POP candidates.

References

1. Euro Chlor (1999): Chlorinated Paraffins Sector Group. Personal communication (Email dated 18/08/99).
2. Anonymous (1999): Unpublished Draft Report of the risk assessment of alkanes, C 14-17, chloro. UK Draft in the framework of the EU existing chemicals programme as of June 1999.
3. Tomy G.T., Fisk A.T., Westmore J.B., Muir D.C.G. (1998): Environmental chemistry and toxicology of polychlorinated *n*-alkanes. Rev. Environ. Contam. Toxicol. 158: 53-128.
4. IPCS (International Programme on Chemical Safety) (1996): Environmental Health Criteria 181 – Chlorinated Paraffins. World Health Organization, Geneva.
5. Anonymous (2000): Unpublished Draft Report of the risk assessment of alkanes, C 14-17, chloro. UK Draft in the framework of the EU existing chemicals programme as of August 2000.
6. Stern, G.A., Tomy, G.T., Muir, D.C.G., Westmore, J.B., Dewailly E., Rosenberg B. (1997) Polychlorinated n-alkanes in aquatic biota and human milk. Convention on Long-range Transboundary Air Pollution (21st session, 16-20 June, 1997, Geneva) Informal in-session document No. 2.
7. Kraemer, W.; Ballschmiter, K. (1987): Detection of a new class of organochlorine compounds in the marine environment: the chlorinated paraffins. Fresenius Z. Anal. Chem. 327:47-48.
8. Froescheis O. (1997): [Analytik und Vorkommen anthropogener schwerflüchtiger Organochlorverbindungen in marinen Organismen aus Oberflächen- und Tiefengewässern des Atlantischen und des Pazifischen Ozeans]. Dissertation, Universtiy of Ulm, Department of Analytical Chemistry and Environmental Chemistry (Prof. Ballschmiter).
9. Bennie D. T., Sullivan C. A. and Maguire R. J. (2000). Occurrence of chlorinated paraffins in beluga whales (*Delphinapterus leucas*) from the St. Lawrence River and rainbow trout (*Oncorhynchus mykiss*) and carp (*Cyprinus carpio*) from Lake Ontario. Water Qual. Res. J. Canada, 35, 263-281.
10. Full text of the Convention: http://www.chem.unep.ch/pops/newlayout/negotiations.htm