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Ecotoxicity assessment of short- and medium-chain chlorinated paraffins used in polyvinyl-chloride products for construction industry

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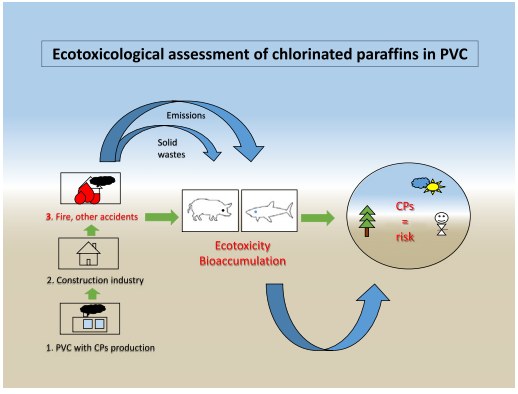
HIGHLIGHTS

- SCCPs and MCCPs used in PVC production are toxic and bioaccumulative POPs.
- In this paper, ecotoxicity of SCCPs and MCCPs is assessed by two LCA methodologies.
- The results indicate potential ecological risks of MCCPs use in some PVC products.
- SCCPs in PVC should better be replaced by some inorganic materials than by MCCPs.

GRAPHICAL ABSTRACT



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ABSTRACT

Short chain chlorinated paraffins (SCCPs) have been commonly used as plasticizers and flame retardants in polyvinyl-chloride (PVC) products for the construction industry. During the last few years the production of SCCPs has been banned or reduced in Europe, Japan, USA, and Canada due to their toxic and bioaccumulative effects but they have been still produced and used under less controlled conditions worldwide. Middle chain chlorinated paraffins (MCCPs) were suggested as a suitable alternative to SCCPs for PVC production instead. In this paper, the ecotoxicity of SCCPs and MCCPs is studied using the methods of potentially affected fraction of species (PAF) and the most sensitive species (MSS). Characterization factors (CFs) are estimated for SCCPs by the PAF method (for MCCPs suitable ecotoxicological indexes are not available) and for MCCPs by the MSS method (for SCCPs PEC values are negligible). Results of the present study indicate that from an ecotoxicological point of view, MCCPs may present similar ecological risks as SCCPs. Therefore, it is recommended both SCCPs and MCCPs not to be used worldwide in PVC products for the construction industry. The most suitable alternative for SCCPs seems to be inorganic compounds but their environmental impacts have not been sufficiently excluded yet.

1. Introduction

Polyvinyl chloride (PVC) is the third most commonly used plastic on the Earth, right after polyethylene and polypropylene. It is produced by the polymerization process from vinylchlorine and for the first time it was synthesized in 1935. More than one half of the world-produced PVC is used in the construction industry for pipes, window and door frames, floor and roof coverings. PVC generally contains various additives for the improvement of its properties, such as fillers, plasticizers, flame retardants, and stabilizers.

Short chain chlorinated paraffins (SCCPs) and middle chain chlorinated paraffins (MCCPs) belong to the most frequently used plasticizers

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and flame retardants at the PVC production worldwide (Glüge et al., 2016). SCCPs are polychlorinated C10–C13-alkanes and MCCPs with C14–C17 have a chlorination degree varying from 30% to 70% (w/w) (EURAR, 2008). Similarly to other halogenated flame retardants, the efficacy of SCCPs and MCCPs consists in interfering with the key reaction of combustion where free hydrogen and hydroxyl radicals react with oxygen. They release halogen atoms into the gaseous phase before the material reaches the ignition temperature. Hydrogen being freed up from the burning material is then fixed with the halogen to form hydrogen-halogen. This process increases caking of the polymer, decreases the amount of volatile flammable products, and thus contributes to retarding of polymer burning (e.g., Petrová et al., 2015). Zhan et al. (2017) observed that SCCPs are evolved from PVC after heating to 100–200 °C; a one-hour thermal treatment caused a release of 1.9–10.7% of embedded SCCPs.

However, SCCPs and MCCPs belong to persistent organic pollutants and are classified as carcinogenic and persistent, bioaccumulative and toxic substances. SCCPs have higher acute and chronic toxicity than MCCPs but MCCPs are more bioaccumulative (ECB, 2008; Glüge et al., 2016; Xia et al., 2017a, 2017b) and more accumulative in the environment (ECB, 2008) due to their higher molecular size and relevant properties. SCCPs were also recommended for further evaluation because of their possible endocrine disruption role (Lassen et al., 2014).

The production and import of SCCPs has been prohibited in the EU (POPRC, 2016), Japan (WCC, 2014), and in the USA and Canada (van Mourik et al., 2016) but MCCPs are currently only listed as "priority substances" for risk assessment under the Council Regulation 793/93/EEC. All chlorinated paraffins are also listed as "priority substances" for the Water Framework Directive. On the international level, MCCPs along with SCCPs are controlled through the OSPAR Convention which protects the marine environment of the north-east Atlantic Ocean.

SCCPs are very stable and their release into the environment, which occurs not only during a fire of building structure but also at a common building usage and PVC processing and recycling (Zhan et al., 2017), will continue yet for a long time after their ban due to the large quantities of PVC produced before. In total, 2,200,000 t of SCCPs have been used between 1935 and 2015 (Glüge et al., 2016). The highest production volumes of SCCPs and MCCPs were reached after 2006, when China scaled up their production from 260,000 t/year in 2006 to 1,000,000 t/year in 2013 (Xu et al., 2014). Currently, SCCPs and MCCPs are still used as plasticizers and flame retardants or in other applications in Asia, Africa and the Americas (with the exception of USA and Canada) without any significant restriction and monitoring (Glüge et al., 2016; van Mourik et al., 2016). China, Russia, and India will thus probably remain the major producers and consumers of SCCPs and MCCPs also in the near future. Therefore, investigations on the ecotoxicity of SCCPs and MCCPs present an actual topic in environmental science and engineering.

Life cycle assessment (LCA) is a method to deal with the environmental impacts associated with products, substances, or service (ISO 14040; ISO 14044). Present LCA softwares include various methodologies for Life Cycle Impact Assessment (LCIA) and they are focusing on preferred impact categories. One of these impact categories is ecotoxicity. Environmental impacts can be assessed for freshwater environment (water or sediment), salt environment (water or sediment), or soil. The effect of comparing products, chemicals, or services in LCA is expressed by characterization factors (CFs) describing and quantifying the cause–effect chain of an emission of a substance to the environment.

In the presented study, two ecotoxicity modeling approaches are used. The first model is based on potentially affected fraction (PAF) of species (e.g., Goedkoop and Spriensma, 1999; Hauschild and Pennington, 2002; Pennington et al., 2004; Salieri et al., 2015) and uses endpoint or/and midpoint level. This concept has been used in the USEtox model (USEtox, 2017), that was developed under the umbrella of the United Nations Environment Program and the Society for Environmental Toxicology and Chemistry (Rosenbaum et al., 2008; Hauschild et al., 2008). The PAF expresses the toxicity put on ecosystems due to the presence of a single chemical or a mixture of chemicals. In many studies based on PAF, the species sensitivity distribution (SSD) concept has been applied. This method uses the available toxicity data for different species with respect to a particular chemical to derive a joint sensitivity distribution, from which the fraction of potentially affected species is determined. Hazard concentration causing x-percentile effect (HC_x) is so derived. The most commonly used levels are HC_5 and HC_{50}. The first affecting 5% of species is considered as protective for the whole community (Smetanová et al., 2014). Characterization factors in the USEtox model are located at endpoint.

The second model is based on the most sensitive species (MSS) and its lowest ecotoxicological index value (lethal concentration, LC_x, or effective concentration, EC_x, where x means that this concentration affects x% of species, or no observed effect concentration, NOEC). This value is compared to modeled substance levels in an affected environment. Characterization factors in the MSS model reflect the damage on the ecosystem quality (species diversity changing) and are located somewhere along the cause-impact pathway, typically at the point after which the environmental mechanism is identical for each environmental flow assigned to that impact category (ISO 14040; ISO 14044).

The PAF- and MSS-based models are applied for the ecotoxicity assessment of SCCPs and MCCPs used in PVC products for the construction industry and the obtained results are discussed. The ecotoxicological data on SCCPs and MCCPs are used for the calculation of both acute and chronic points, based on the toxicity data for different trophic levels. Limitations of both types of models are discussed and possible improvements are proposed. Alternatives to SCCPs and MCCPs for PVC products are suggested as well.

2. Methods

2.1. Concept of potentially affected fraction (PAF) of species

The most widespread endpoint model USEtox (USEtox, 2017) estimates the characterization factor (CF) of a substance for the impact category of freshwater ecotoxicity as:

$$CF = EF \times FF \times XF \quad (1)$$

where EF ($PAF \cdot m^3 \cdot kg^{-1}$) is the effect factor that represents the ecotoxicity and which is expressed in terms of potentially affected fraction of species, FF (day) is the fate factor which expresses the residence time of a substance in a particular environmental compartment (freshwater), XF (dimensionless) is the exposure factor which is the fraction of a chemical dissolved in freshwater (Rosenbaum et al., 2008; Larsen and Hauschild, 2007a, 2007b).

2.1.1. Effect factor

The effect factor can be generally defined as

$$EF = 0.5/HC50_{EC/LC50}, \quad (2)$$

where $HC50_{EC/LC50}$ is the concentration at which 50% of included species is exposed above their chronic EC_{50} or LC_{50} level. In this study, the EF of SCCPs was estimated using ecotoxicity values from previously published studies on freshwater organisms representing the three trophic levels recommended by the USEtox model (algae, crustacean, fish) (Larsen and Hauschild, 2007b). The ecotoxicity data for PAF derivation were collected from IUCLID Chemical Data Sheets and complemented with published data (Table 1). Only acute or chronic LC/EC_{50} values for the endpoints of growth, biomass, mortality, and immobilization from tests were used. In the case of multiple EC_{50} values per one species (*D. magna*, see Table 1), the geometric mean was used. Acute LC_{50} values were divided by 2 (Rosenbaum et al., 2008). Chronic NOEC data were