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Emission inventory and provincial distribution of short-chain chlorinated paraffins in China

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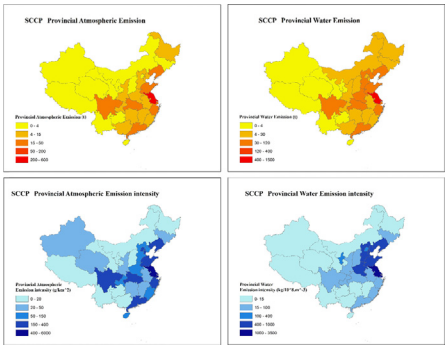
HIGHLIGHTS

- China's major consumer sectors of CP were identified.
- SCCP emissions were estimated at national level by bottom-up method.
- The provincial emission distribution identified key emission areas in China.

GRAPHICAL ABSTRACT



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ABSTRACT

Chlorinated paraffins (CPs) are used as flame retardants, plasticizers, and metalworking fluids, which have varying contents of toxic short-chain chlorinated paraffins (SCCPs). Based on the study of several relevant production and consumption sectors, this paper classifies the consumption of CPs among sectors and provides an emission inventory and the provincial emission distribution of SCCPs in China in 2010–2014 based on the consumption patterns and emission factors of each sector. The total emissions of SCCPs in China in 2014 were 3083.88 tons, with emissions to the atmosphere and water accounting for 894.81 tons and 2189.07 tons, respectively. The largest emission source was from metalworking fluids, with total emissions of 2459.12 tons, of which 756.65 tons went to the atmosphere and 1702.47 tons to water. Our results show that SCCP emissions were mainly concentrated in the eastern, more developed regions and that Jiangsu Province was the biggest producer in China, with total emissions of 1853.06 tons, of which 562.61 tons were to the atmosphere and 1290.46 tons to water.

1. Introduction

Chlorinated paraffins (CPs) are a group of derivatives synthesized from the chlorination of paraffin hydrocarbons, with mass fractions of chlorine between 30% and 70%, and carbon chain lengths from 10 to 30. CPs are colorless or yellowish liquids or solids. With increases in

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the degree of chlorination, its viscosity increases and volatility decreases. In the early 1930s, CPs came into use in metalworking fluid due to their extreme pressure tolerance, and they are now used extensively as flame retardants and polyvinyl chloride (PVC) plasticizers used to produce cable, flooring, hoses, artificial leather, and rubber products and as additives to paint, lubricants and other industrial products.

Short-chain chlorinated paraffins (SCCPs) are chlorinated derivatives of n-alkanes with carbon chain lengths between 10 and 13, usually as mixtures containing various carbon chain lengths and degrees of chlorination. At room temperature, SCCPs are light yellow or colorless viscous liquids with log octanol/water partition coefficient (Kow) values between 4.8 and 7.6 (Sijm and Sinnige, 1995) and bioconcentration factors (BAFs) >5000 (POPRC, 2007). Many toxicological experiments have confirmed that they exhibit some carcinogenicity (Fisk et al., 1999; Serrone et al., 1987).

SCCP concentrations in environmental media have been reported in different countries and regions, including the Arctic, Canada, Norway, Japan and the UK (Borgen et al., 2000; Borgen et al., 2002; Marvin et al., 2003; Borgen et al., 2003; Li et al., 2012; Barber et al., 2005). The monitoring results revealed that SCCPs exist in different media and pose a potential ecological threat to the environment. However, studies have shown that there are no natural sources of SCCPs, indicating that they originate from the production and consumption of related industrial products. SCCPs are now considered groups of candidate persistent organic pollutants (POPs) by the Persistent Organic Pollutants Review Committee (POPRC) and it has been proposed to formally include them in the Stockholm Convention (SC) on POPs; their production and consumption in the United States, the European Union and Japan are under strict control. Researchers in these countries have investigated the production and consumption of SCCPs and the management of risks associated with them, but few studies have been conducted on SCCPs in China.

Today, China is the world's largest producer and consumer of CPs. As China's CP market is unregulated, with no clear division of product grades, specifications, or performance, mixtures always contain some toxic short-chain components. It can be predicted that China's high CP consumption will lead to a considerable amount of SCCP emissions. Therefore, studies on the release of SCCPs are urgently needed to support risk assessments and the phasing out of SCCPs, as well as to comprehensively implement the Stockholm Convention.

This study applied a bottom-up method to construct a historical inventory of Chinese emissions and the provincial distribution of SCCPs based on research in CP-related economic sectors. First, major consumer sectors were identified, and the annual national emissions of SCCPs were inventoried from 2010 to 2014. Then, a provincial distribution was constructed to identify high emission areas in China. Finally, the uncertainty associated with this research was assessed.

2. Methodology

Most SCCP emissions occur during processes related to CP production and consumption. According to industrial research on CPs conducted by the China National Chemical Economic and Technical Development Center (China National Chemical Economic and Technical Development Center, 2008; China National Chemical Information Center, 2007–2015), the major uses of CPs in China are in plasticizers, flame retardants, and metalworking fluids. A small amount of CPs is used in the production of leather fatliquor and printing ink, which together account for about 6% of the total consumption; however, this proportion continues to decrease because of rapid development in the sectors of flame retardants and plasticizers. In this study, CP consumption was found to occur mainly in three sectors: flame retardants, plasticizers, and metalworking fluids.

2.1. Estimation of SCCP consumption

Chinese CP products are not characterized based on alkane chain length, but by chlorine content, and thus it is difficult to estimate the consumption of SCCPs by different sectors. According to research on CPs by the China National Chemical Economic and Technical Development Center (China National Chemical Economic and Technical Development Center, 2008; China National Chemical Information Center, 2007–2015), SCCP content varies based on the raw materials and processes used in CP production, which differ among sectors. For example, CP produced from hard wax using the aqueous-phase suspension method does not contain SCCPs, whereas that produced by hard wax and liquid paraffin in the thermal chlorination process does. Imported paraffin wax also contains SCCPs.

2.1.1. SCCPs in PVC plasticizers and flame retardants

Because there is no domestic restriction on the short-chain content of CP products, small enterprises tend to use relatively inexpensive raw materials, resulting in a relatively high content of SCCP. In general, the short-chain content of CP products is about 6%, whereas the proportion in products from relatively small manufacturers can reach 10% to 20% (Shen et al., 2016), as confirmed by data from the China Chlor-Alkali Industry Association and our research. In this study, considering production costs and processes used by different sectors, the SCCP content of PVC plasticizers and flame retardants was set at 20% based on the worst-case scenario.

2.1.2. SCCPs in metalworking fluids

According to the survey conducted here, about 60% of the total CP consumption in this sector is used for work that does not need high precision, and the proportion of short-chain components in these products can reach 50%. The other 40% of products, of which short-chain compounds account for about 2%, are mainly used in harsh and high precision conditions. Accordingly, the SCCP content is described by Eq. (1):

$$C = \sum \mathrm{PC}_i \times \mathrm{CS}_i \quad (1)$$

where C is the average SCCP content in the metalworking fluids sector, PC_i is the proportion of CP consumption from part i, and CS_i is the content of SCCP from part i. Thus, the SCCP content in the metalworking fluids sector is 30.8%.

2.2. Calculation of national SCCP emissions

This study classified emission sources into seven categories; production of CP, synthesis of flame retardants, synthesis of PVC plasticizers, use of flame retardants, use of PVC plasticizers, synthesis of metalworking fluids and use of metalworking fluids. We used emission factor data

Table 1
Annual emission factors.

Emission Source	Atmosphere	Water
Production of CPs	0	0.3%
Synthesis of flame retardants	Synthesis stage: 0.005% Transformation stage:0.025%	Raw material processing stage: 0.01% Synthesis stage: 0.005% Transformation stage: 0.025%
Use of flame retardants	0.0029%	Indoor: 0.0029% Outdoor: 0.016%
Synthesis of PVC plasticizers	0.1%	0.05%
Use of PVC plasticizers	0.0029%	Indoor: 0.0029% Outdoor: 0.016%
Synthesis of metalworking fluids	0	0.25%
Use of metalworking fluids	8%	18%

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