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Contamination of short-chain chlorinated paraffins to the biotic and abiotic environments in the Bohai Sea☆

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ABSTRACT

Short-chain chlorinated paraffins (SCCPs) have been produced and emitted intensively around the Bohai Sea, potentially causing risks to this unique ecosystem and one of primary fishery resources in China and busiest seaways in the world. Little is known about fate, cycling, and sources of SCCPs in the Bohai Sea biotic and abiotic environment. In this study, we combined a marine food web model with a comprehensive atmospheric transport-multiple phase exchange model to quantify SCCPs in the biotic and abiotic environment in the Bohai Sea. We performed multiple modeling scenario investigations to examine SCCP levels in water, sediment, and phytoplankton. We assessed numerically dry and wet depositions, biomagnification and bioaccumulation of SCCPs in the Bohai Sea marine food web. Results showed declining SCCP levels in water and sediment with increasing distance from the coastline, and so do dry and wet depositions. The net deposition overwhelmed the water-air exchange of SCCPs due to their current use in China, though the diffusive gas deposition fluctuated monthly subject to mean wind speed and temperature. A risk assessment manifests that SCCPs levels in the Bohai Sea fish species are at present not posing risks to the residents in the Bohai Sea Rim region. We identified that the SCCP emission sources in the south of the Bohai Sea made a primary contribution to its loadings to the seawater and fish contamination associated with the East Asian summer monsoon. In contrast, the SCCP emissions from the north and northwest regions of the Bohai Sea were major sources contributing to their loading and contamination to Bohai Sea food web during the wintertime, potentially driven by the East Asian winter monsoon.

1. Introduction

Chlorinated paraffins (CPs), also known as polychlorinated *n*-alkanes with chlorine degree ranging from 30% to 70% by mass, are a complex mixture of thousands of isomers, diastereomers, and enantiomers (Feo et al., 2009). CPs can be divided into short (SCCPs, C10-C13), medium (MCCPs, C14-17), and long chain CPs (LCCPs, >17) according to their carbon chain length (Wei et al., 2016). The chemical stability and high toxicity of SCCPs render them to be bioaccumulated and biomagnified through food web (Iozza et al., 2008), causing adverse health risks to humans (Hilger et al., 2013). SCCPs have been used widely as additives in metal-working fluids, flame retardants, plasticizers, paints, leathers and sealants since the 1930s. There has been ample evidence that SCCPs have been detected in all biospheric compartments including human tissues (Harada et al., 2011), raising considerable attention in the scientific community (de Boer et al., 2010; van Mourik et al., 2016; Wei et al., 2016). Given their bioaccumulation and toxicity, SCCPs have been added to the toxic release inventory by the European Union (EU), Japan, Canada, and the United States (POPRC, 2015). As new persistent organic pollutants (POPs), SCCPs have been amended to Annex A (2017) by the Stockholm Convention (POPRC, 2017). China is the largest producer and consumer of CPs worldwide, producing about 15% of the global total CP production

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in 2013 (WCC, 2014; van Mourik et al., 2016). Jiang et al. (2017) reported that 20–30% of global CPs production from 2007 to 2013 was produced by China. Since the use of SCCPs in China has not been regulated, their large production and strong emissions may pose significant risks to the biotic and abiotic environment in China. To assess such eco-environmental risks to SCCPs, extensive field sampling of this group of toxic chemicals is needed. Due to difficulties in sampling methods and cost in lab analyses of SCCPs in large-scale field measurements, measured SCCP concentrations in different environmental compartments on a regional and national scale across China are still lacking, although a number of SCCP field samplings were taken in local urban and suburb sites in eastern and southern China (Chen et al., 2011; van Mourik et al., 2016; Wei et al., 2016; Zeng et al., 2011). As an alternative, models with sufficient validation against measured data can provide very useful tools to assess spatial and temporal distribution, predict environmental levels and fate, and quantify source-receptor relationships of SCCPs and other organic chemicals (Diefenbacher et al., 2015; Gawor and Wania, 2013; Vulykh et al., 2007).

The Bohai Sea is a unique semi-enclosed inner sea in Northern China, characterized by poor seawater exchange and recycling. The Bohai Sea watershed is one of the most populated and industrialized regions in China. With rapid economic development and urbanization over the past decades around the Bohai Sea, the marine ecosystem has been heavily contaminated by the inputs and discharge of toxic chemicals through atmosphere, runoff and circumjacent rivers, such as nitrogen and phosphate which have resulted in eutrophication in the Bohai Sea (Zeng et al., 2013). Among those toxic chemicals, SCCPs have been produced near the Bohai Sea for years. Ma et al. (2014) reported that SCCP levels in the sediment of the Bohai Sea ranged from 97.4 ng/g dry weight (dw) to 1756.7 ng/g dw, considerably higher than their levels in marine sediments in Japan, ranging from 4.9 to 484.4 ng/g dw (Iino et al., 2005). Yuan et al. (2012) found the highest $\sum$SCCPs in the collected mollusks with a mean level of 2830 ng/g dw near Tianjin, a metropolis city on the shore of the Bohai Sea. The environmental occurrence and distribution of SCCPs in sediment samples revealed a decreasing spatial trend with increasing distance away from the coastline to the sea, depending on the proximity of sampling sites to urban or rural areas (Gao et al., 2012; Zeng et al., 2012).

In the bottom of Bohai Sea food web, benthic invertebrate species residing on the sediments are crucial for the Bohai Sea marine food chain (Ma et al., 2014; Yuan et al., 2012). Sediments provide stationary “end points” where SCCPs may reside for longer periods. This has been demonstrated by SCCP bioaccumulation in organisms and biomagnification through the food web in the marine ecosystem (Houde et al., 2008; Reth et al., 2006; Yuan et al., 2012; Zeng et al., 2011) because of their high lipophilicity (log K_{OW}: 4.8–8.1) (Fisk et al., 2000) and resistance to metabolism (Hilger et al., 2013). For instance, mollusks and shellfish are invertebrate benthic organisms and water-respiring filter feeders which have been found to exhibit high bioaccumulation capacity for POPs (Tanabe et al., 2000). Given that contamination of SCCPs has occurred in the Bohai Sea Rim, reaching the seawater and sediment far from the coastline and their sources (Zeng et al., 2012; Zhao et al., 2013), concerns should be raised because these toxic chemicals may enter the human food chain. However, presently the knowledge of spatial and temporal distribution and pathways of SCCPs across the Bohai Sea and its sediments are still very poor due to the lack of field sampling data.

In the present study, a model framework including atmospheric transport, water-air, soil-air, water-sediment, phytoplankton-water exchange, and marine food web model was employed to simulate spatial distribution of SCCPs in the air, sediment, water, and their exchange fluxes around and in the Bohai Sea. The objectives aim at (1) quantitatively assessing the contribution of primary emission sources of SCCPs in China to its contamination to the Bohai Sea marine ecosystem and food web; (2) unveiling the source-receptor relationships of SCCPs and SCCP inputs from different areas over China via atmospheric transport to water and sediments; and (3) evaluating the potential risks of the marine food web and human to SCCP contamination.

2. Materials and methods

2.1. Gridded SCCPs emission inventory

The gridded SCCP emission inventory with a 1/4° longitude by 1/4° latitude resolution in China was used in this modeling investigation of SCCP contamination in the Bohai Sea marine environment and food web. This inventory takes into consideration of all primary emission sources of SCCPs, including the additive in metal cutting fluids, the production of CPs, plasticizers, flame retardants, and net import, respectively. The details of this inventory can be found in Jiang et al. (2017). Fig. S1 of Supplementary Information (SI) illustrates gridded mean SCCP emissions in China averaged over 2008 to 2012.

2.2. CanMETOP model

The model framework applied in the present study is a combination of an atmospheric transport model coupled with water-air, soil-air, water-sediment, and phytoplankton-water exchange modules, and a marine food web model. This model framework is an extension of the Canadian Model for Environmental Transport of Organochlorine Pesticides (CanMETOP) which is a three-dimensional atmospheric transport model coupled with a dynamic, three soil layers, fugacity-based soil-air exchange model, and a two-thin film model for water-air exchange of targeted chemicals. The model has been applied extensively in simulating atmospheric transport and deposition, as well as the multi-phase exchange of POPs among different environmental compartments (Daggupaty and Ma, 2011; Huang et al., 2016; Li et al., 2010; Tian et al., 2009). The model contains 14 vertical levels at 0, 1.5, 3.9, 10, 100, 350, 700, 1200, 2000, 3000, 5000, 7000, 9000, and 11,000 m height, with 1/4° latitude by 1/4° longitude horizontal resolution. Meteorological data (including winds, atmospheric pressure, temperature, precipitation, etc.) used the 6-hourly objectively analyzed data from the 1° × 1° latitude/longitude National Centers for Environmental Prediction (NCEP) Final Operational Global Analysis (http://dss.ucar.edu/datasets/ds083.2/). These data were interpolated into CanMETOP model grids in the horizontal (0.25° × 0.25° lat/lon) and vertical directions, and the 20-min time step length.

In the updated model framework, the CanMETOP model was extended to include water-sediment and water-phytoplankton exchange modules for SCCPs. The water-sediment exchange was simulated by making use of a mass balance model (Mackay et al., 1994). The details of this model are described in SI. Considering increasing degree of eutrophication which has enhanced phytoplankton biomasses in the Bohai Sea, particularly since the late 1990s (Sun et al., 2011), we implemented a phytoplankton-water exchange model for organic chemicals to estimate SCCP levels in phytoplankton (Mayumi and Handoh, 2009). The model was used to quantify the influence of the phytoplankton-water exchange on the transport and fate of SCCPs in the marine environment (see SI). In a marine ecosystem, phytoplankton is often laid on the bottom tropic level of marine food web and plays a key role in the transfer of organic chemicals from water to fish (Skei et al., 2000; Wallberg and Andersson, 2000).