

Medium-chain and long-chain chlorinated paraffin products predominate in Swedish coastal sediment cores over the past 50 years.

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Introduction

Chlorinated paraffins (CPs) are complex mixtures of polychlorinated straight alkanes. They have been commonly used as lubricants, plasticizers, flame retardants and metal cutting fluids for decades. CPs are divided into short chain (C₁₀₋₁₃, SCCPs), medium chain (C₁₄₋₁₇, MCCPs), and long chain (C₁₈₊, LCCPs) products, according to the alkane-chain-length range [1]. SCCPs, MCCPs and LCCPs are considered toxic to many aquatic organisms such as invertebrates [2]. SCCPs were proposed to be included in the Stockholm Convention list of persistent organic pollutants (POPs) [3]. MCCPs meet the criteria for substances of very high concern as defined by REACH [4].

Compared to SCCPs, MCCPs and LCCPs have received less attention. However, recent studies showed that MCCPs and/or LCCPs were predominant CPs in sewage sludge [5], soil [6] and indoor dust [7] in many countries. Whether these CPs, especially LCCPs, are “new” contaminants in the environment is unclear. In this study, we measured CPs with alkane-chain lengths ranging from C₉ to C₃₆ in a sediment core collected from the Baltic Sea coast for a historical profile of CP pollution in Sweden.

Materials and methods

Wastewater treatment plants are typical sinks and sources of CPs.[8] Sediment cores from the Baltic Sea were collected in September 2016 near Himmerfjärden wastewater treatment plant (59°04'03.6"N 17°42'25.9"E) at a depth of c.a. 20 – 50 m using a gravity corer with a diameter of 58 mm. The wastewater treatment plant serves about 340 000 persons of the southern Stockholm's metropolitan area. One core was used for analytical method validation and preliminary testing. Then a 1.2-m core was used to rebuild a historical profile of CP pollution. The cores were cut into 2.5 cm slices and stored in Whirl-Pak® sampling bags in a -20 °C freezer before dating. The sediment cores were dated by ¹³⁷Cs and ²¹⁰Pb analysis [9]. The average sedimentation rates were 0.82 – 0.98 cm per year. The extraction and cleanup process for CP analysis was adopted from previous studies [7, 10]. Briefly, approximately 10 g of freeze-dried samples was spiked with ¹³C_{10-1,5,5,6,6,10}-hexachlorodecane as the internal standard and extracted using accelerated solvent extraction (ASE 300; Dionex Europe, Leeds, UK). The extracts were blown to near dryness with nitrogen, sulfur was removed using activated copper and then cleaned-up on a multilayer SPE column. The eluent was reconstituted in 100 µL isooctane. 20 ng Dechlorane-603 was used as volumetric standard.

Instrumental Analysis: Samples were directly injected into APCI-QTOF-MS (QTOF Premier, Waters, UK). Instrument settings have been described previously [11] and were applied with several adjustments [12]. The observed resolution was 8000 – 9000. CP congener groups from C₉Cl₃ to C₃₆Cl₁₅ were considered to form a congener group pattern.

Quantification: CP congener group patterns of a set of CP technical products ($n = 65$) were initially analyzed, and a sub-set of 16 products were selected for quantification in this study, consisting of 5 SCCPs, 6 MCCPs and 5 LCCPs. The CP congener group pattern of each sample was reconstructed by a deconvolution algorithm from

CP patterns of the selected products. In this study, CP patterns in the sediment samples were satisfactorily reconstructed ($R^2 > 0.80$). Relative contributions of the products were then used to calculate instrument response factors of SCCPs, MCCPs and LCCPs in the sample. A detailed deconvolution procedure has been given in Bogdal et al [11]. The limits of quantification (LOQ) was defined based on the blank plus ten times the standard deviation (SD), which is 1.4 and 6.5 ng/g dry sediment for SCCPs and MCCPs, respectively. LCCPs were undetectable in the blank.

Results and discussion

Total CP concentrations (Σ CPs) in the sediment core are shown in Figure 1. Σ CPs were above LOQ in the sediment section representing the year 1960 and increased to the maximum concentration of 48 ng/g d.w. in 1991. Σ CPs decreased to 15 ng/g d.w. in the surface sediment (representing the year 2015). Σ CPs were, in general, lower than in sediment from Switzerland [13], China and Japan [14], which may be due to comparably lower use of CPs in the studied area. The historical trend of Σ CPs in the sediment core is consistent with statistics on imported amounts of CPs to Sweden, which showed that the highest annual import of Σ CPs was 4800 tons in 1991 [15]. Since there is no CP production in Sweden [15], the import amount indicates the amounts of CPs in use.

LCCPs were the predominant CPs before 1991, making up c.a. 60 % of total CPs. After 1991, MCCPs became predominant, making up c.a. 70 % of total CPs. The results were also supported by a recent study in which CPs in dust from Sweden were predominated by LCCPs [7]. In all sections of the sediment cores, SCCPs were less than 20 % of total CPs with an average of 10 %. This is consistent with the import of CPs in Sweden, where SCCPs were on average 10 % of total CPs imported between 1990 – 2014 [15]. CP compositions in the sediment core show that large amounts of MCCPs and LCCPs have been emitted into the local environment for a long time.

Figure 2 shows a congener group pattern of CPs in a sediment section representing the year 1960. $C_9 - C_{36}$ CPs were identified in the section, with C_{24} as the dominant alkane-chain-length group. These CPs, consisting of SCCPs, MCCPs, LCCPs and C_9 CPs, appear to have persisted in the sediment for c.a. 50 years.

This study indicates that CP pollution in Sweden is predominated by MCCP and/or LCCP products. Whether MCCPs and LCCPs pose a risk to the environment, in particular marine sediment ecosystem, is not clear, and requires further study.

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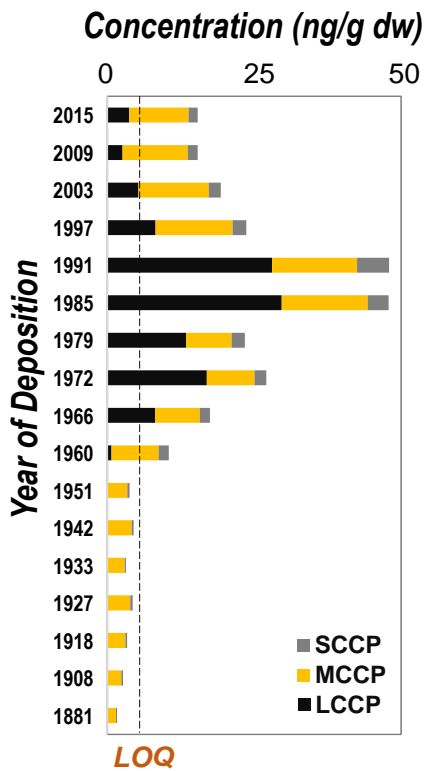


Figure 1. Historical time trend of SCCP, MCCP and LCCP concentrations in a sediment core from the Baltic Sea.

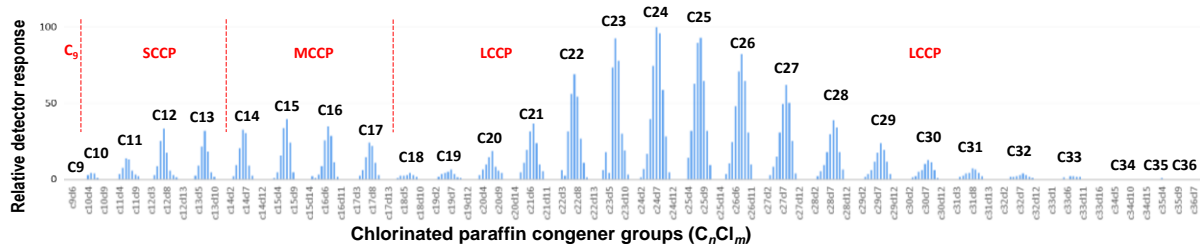


Figure 2. Chlorinated paraffin congener group pattern in a 50-year-old sediment section.