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# Chlorinated Paraffins in Sediment Cores Collected from the Baltic Sea and the Kattegatt

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<b>Nyckelord för plats</b> the Bothnian Sea (Bottenhavet), the Baltic Proper (Egentliga Östersjön), the Kattegatt	
<b>Nyckelord för ämne</b> chlorinated paraffins (kloroparaffiner), SCCPs, MCCPs, LCCPs, total organic carbon (TOC)	
<b>Tidpunkt för insamling av underlagsdata</b> 2020	
<b>Sammanfattning</b> Chlorinated paraffins (CPs) are widely used industrial chemicals e.g., as metal working fluids, rubber additives, flame retardants, etc. These chemicals are multiconstituent mixtures, which are categorized into short-chain (SCCPs), medium-chain (MCCPs), and long-chain mixtures (LCCPs). Only SCCPs have been under regulation as POPs. Spatial and temporal trends of SCCPs, MCCPs, and LCCPs in Swedish marine environment were investigated in the present report. Three sediment cores were collected from the Baltic Sea and from the Kattegatt. CPs and TOC were analyzed in the dated sediment sections and compared with the other three sediment cores collected from the Swedish coastal line in a previous study. Sediments nearby industrial areas showed the highest concentrations of CPs (up to 1400 ng/g d.w.), over 80% of which were MCCPs. The highest concentration of SCCPs (170 ng/g d.w.) was found in the sediments nearby a smelter as well as a recycling facility for electric wastes. Over the past decades, decreasing trends of CPs or relatively consistent levels of MCCPs and LCCPs were found in most sediment cores. However, increasing trends of SCCPs were shown in the sediment cores from the Bothnian Sea and Kattegatt even though the use of SCCPs has been restricted in Sweden and Denmark since 1991. Further studies on source identification are warranted.	

## Background

Chlorinated paraffins (CPs) are multiconstituent industrial products. CPs are widely used as cutting fluids and fluids for modelling metals, rubber additives, filling materials, flame retardants, etc. Their annual production capability of CPs worldwide is around two million tons nowadays.<sup>1</sup> Sweden has no local production of CPs, and therefore all CPs used are imported. The annual importation volume reached c.a. 4800 metric tons in 1991<sup>2</sup> and decreased to 152.2 metric tons in 2019 (excluding CPs imported in products such as electronics).<sup>3</sup>

CPs are complex mixtures of polychlorinated *n*-alkanes, the chemical formula of which are  $C_nH_{2n+2-m}Cl_m$ . Their industrial products are usually classified based on the paraffin carbon numbers into short-chain ( $n = 10 - 13$ , SCCPs), medium-chain ( $n = 14 - 17$ , MCCPs), and long-chain CPs ( $n > 17$ , LCCPs). Some products may contain very-short-chain impurities ( $n < 10$ , vSCCPs).<sup>4</sup> SCCPs are the first CP class that are listed as Persistent Organic Pollutants (POPs) in 2017. Current regulatory actions are extending to MCCPs which are being considered as POPs candidate.<sup>5</sup>

Recently, CPs from vSCCPs to LCCPs have been found in Baltic Sea biota, the concentrations of which were similar to or higher than several legacy POPs,<sup>6</sup> highlighting the need of studying CP pollution in this aquatic environment. In a previous study, three sediment cores were collected from the Swedish Baltic coast, while no data so far are available from offshore areas or the west coast of Sweden.

In this project, we filled in the data gap by analyzing CPs in three sediment cores from the offshore Baltic Sea and from the Kattegatt. This data provides a spatial distribution of CPs together with the coastal sediment analyzed previously. By analyzing CPs in selected sediment sections that had been dated, the historical pollution trends were reconstructed in the water bodies surrounding Sweden.

## Samples, materials, and methods

Three sediment cores were collected from the Bothnian Sea and the Baltic Proper, located in the Baltic Sea as well as from the Kattegatt in 2020. The cores were sliced into 1 cm sections. Some sediment sections were mixed to get enough material for CP analysis. The samples were then freeze-dried, and the water content were measured (Table 1). Total organic carbon (TOC) was determined using dry combustion and EA-IRMS. Average deposition rates were measured previously using Pb-210.

**Table 1.** Sediment core information

Site	Deposition rate measured in 2014 (cm/yr)	Water content (%)	Total organic carbon range (TOC, %)
Bothnian Sea, Baltic Sea	$0.16 \pm 0.01$	$80.6 \pm 5.4$	(2.73 – 5.09)
Baltic Proper, Baltic Sea	$1.03 \pm 0.37$	$88.6 \pm 9.1$	(2.10 – 13.6)
Kattegatt, Swedish west coast	$0.62 \pm 0.15$	$61.4 \pm 7.6$	(1.28 – 2.01)

CPs were analyzed using the same method as in Yuan et al. (2017)<sup>7</sup> with minor modifications. Briefly, approximately 6 g of freeze-dried sediment was spiked with 10 ng <sup>13</sup>C-1,5,5,6,6,10-hexachlorodecane (Cambridge Isotope Laboratories, Andover, MA U.S.A.) as internal standard and extracted by accelerated solvent

extraction (ASE 300; Dionex Europe, Leeds, UK). The extracts were concentrated, and then treated by activated copper and a multilayer SPE column. The eluent was reconstituted in dichloromethane, and 10 ng of  $^{13}\text{C}$ -1,1,1,3,10,12,12,12-octachlorododecane (Cambridge Isotope Laboratories, Andover, MA, U.S.A.) was added as a volumetric standard prior to instrumental analysis.

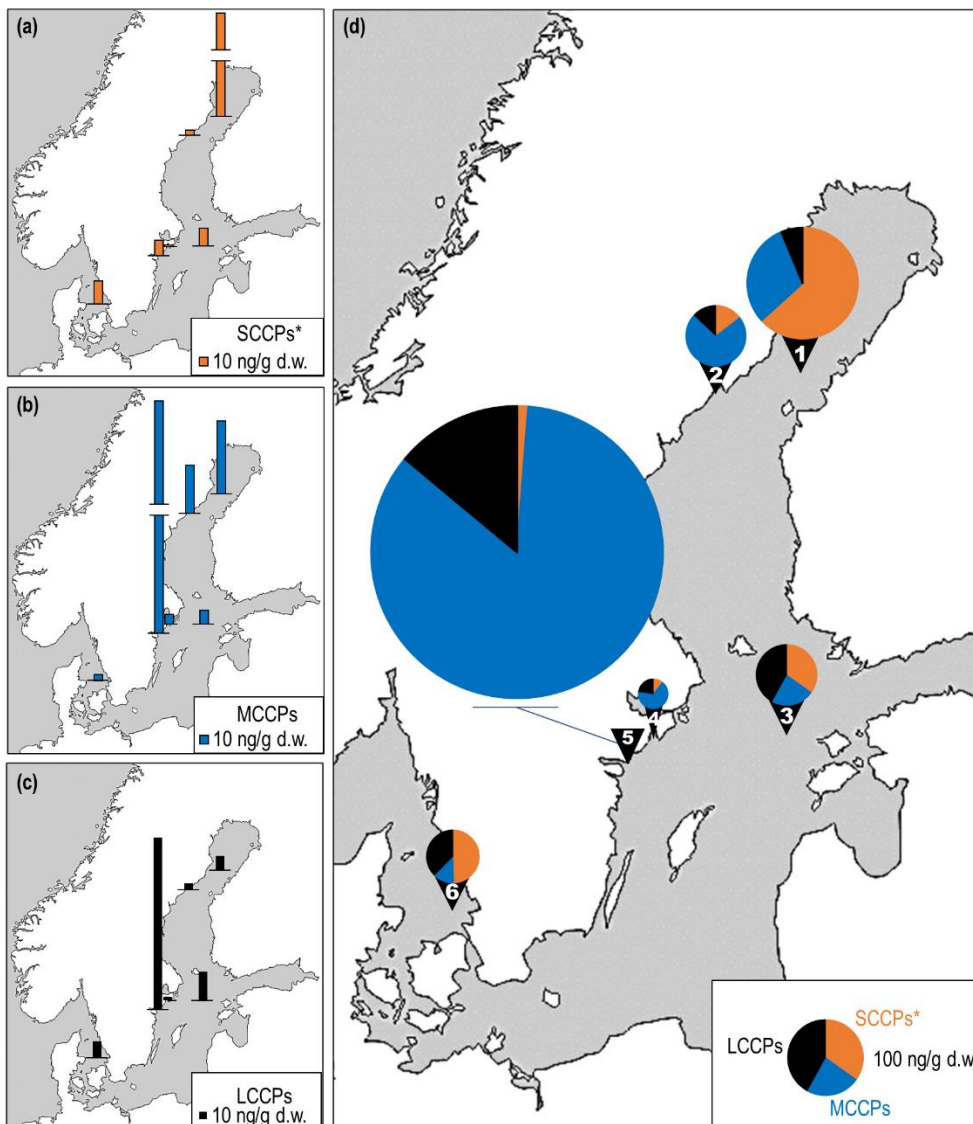
UPLC-APCI-Orbitrap-MS (Q Exactive, Thermo Fisher Scientific, San Jose) was used for analysis of CP homologues ( $\text{C}_n\text{Cl}_m$ ) with  $n = 6\text{--}36$  and  $m \geq 2$ . Quantification of vSCCPs, SCCPs, MCCPs, and LCCPs was based on homologue profile reconstruction. The recovery of the surrogate standard was  $94 \pm 8\%$ . Two sediment sections representing pre-industrial age were used for field blanks. Four new containers were rinsed by acetone, and the rinsing solvent was collected and concentrated as a container blank. A procedural blank was included with each batch of samples prepared. The method detection limit (MDL) of each CP class was defined as the mean procedural blank plus 3 times the standard deviation, divided by sample dry mass (d.w.). The average MDLs were 0.67, 6.2, 3.8, and 0.19 ng/g d.w. for vSCCPs, SCCPs, MCCPs, and LCCPs, respectively, while the MDLs and the results of individual samples can be found on SGU Datavärdsrapport för miljö-gifter.<sup>8</sup> Both the field blanks and the container blank were below the MDLs for all CP classes.

## Results and discussion

**Spatial tendencies of CPs.** The total concentrations of CPs in core-top sediments were plotted in Figure 1. The highest concentrations of CPs were found in the sediment collected from Oxelösund, the Baltic Proper (1400 ng/g d.w.)<sup>7</sup> and from the Bothnian Sea (300 ng/g d.w.). The sampling site at Oxelösund was nearby a metal working factory, while the site in the Bothnian Sea was relatively close to a smelter Rönnskärsverken as well as a recycling facility for electronic waste. This suggests that industrial activities could be major sources of CP emissions. Mediatedly high levels of CPs were found in the sediment from the Baltic Proper. The sediment from the Baltic Proper has the highest TOC values and tend to be sinks of many pollutants.

The concentrations of vSCCPs were added to the concentrations of SCCPs, in order to be consistent with the sediment results in the previous study.<sup>7</sup> The highest concentration of SCCPs was found in the core-top sediment from the Bothnian Sea (170 ng/g d.w.). Furthermore, SCCPs were the dominant CP class there, which contributed to 58% of the total concentration of CPs. Since SCCPs were not regulated as POPs until 2017, the SCCPs found in the sediment from the Bothnian Sea might be from the recycled electronic waste that were generated before the ban of SCCPs. The proportions of SCCPs were very low in the sediments nearby the metal working factory (Oxelösund, 1.3% of the total CPs) and wood-related factory (Rundvik, 4.8% of the total CPs), reflecting the enforcement of chemical regulation.

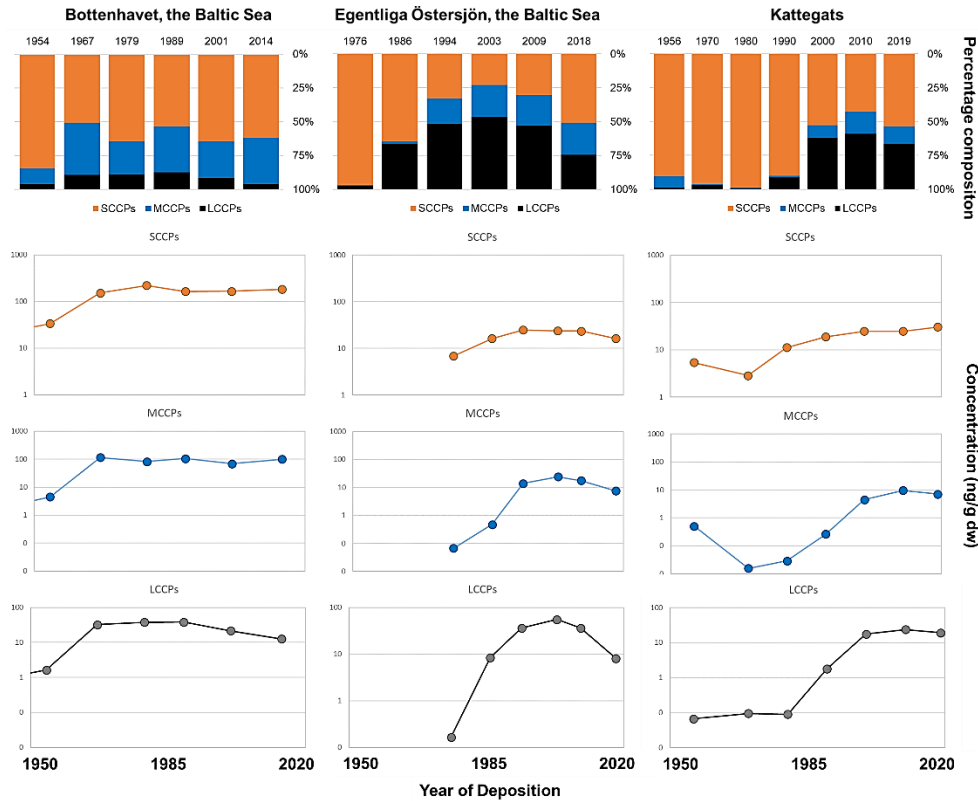
MCCPs and LCCPs are current-use CPs. MCCPs predominated in the sediments nearby by the metal working factory (Oxelösund, 85% of the total CPs) and wood-related factory (Rundvik, 88% of the total CPs), reflecting their usage in the industrial activities in large quantities. LCCPs were detected in all the core-top sediments. LCCPs were more abundant than MCCPs in the sediment from the Baltic Proper and Kattegatt. Predominant LCCPs were also found in a killer whale collected from Kattegatt.<sup>9</sup> The sources of LCCPs at those two sites are unclear.



**Figure 1.** Spatial distribution of concentrations and compositions of chlorinated paraffins in core-top sediments from the Baltic Sea: (a) total concentrations\* of vSCCPs and SCCPs, (b) concentrations of MCCPs, (c) concentrations of LCCPs, and (d) CP compositions. The circle areas of (d) are proportional to the CP concentrations. Sampling sites: ① Bothnian Sea ② Rundvik, ③ Baltic Proper ④ Himmerfjärden, ⑤ Oxelösund, and ⑥ Kattegatt.

**Temporal trends of CPs.** The temporal trends of SCCPs, MCCPs, and LCCPs as well as their percentage composition were plotted in Figure 2. The decreasing trends of SCCPs, MCCPs, and LCCPs in the sediment core from the Baltic Proper were generally similar to the trends found in the core collected from Himmerfjärden. It is worth noting that the concentrations of SCCPs in the cores from the Bothnian Sea and Kattegatt were both increasing over the past 30 years. The increasing trend of SCCPs found in the Bothnian Sea might be due to the recycling activities of electric waste. However, it is unknown why the concentrations of SCCPs also increased in the sediment from Kattegatt even though the use of SCCPs has been restricted in both Denmark and Sweden since 1991. The potential sources of SCCPs

could be possibly identified with further analysis of samples nearby local industrial areas and wastewater treatment facilities.



**Figure 2.** Historical trends of SCCP, MCCP, and LCCP concentrations and percentage compositions of three CP classes in the sediment cores analyzed in the current report. CP concentrations are shown using the logarithmic scale.

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