

Levels Of Chlorinated Paraffins in North and Baltic Sea Sediments

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Introduction

The determination of environmental levels of chlorinated paraffins (CPs) is a challenge due to the high complexity of the applied congener mixtures. Formulations with varying carbon chain lengths between C₁₀ and C₃₀ and chlorination degrees between 30 and 70%^[1] contain several thousands of isomers and homologues.

Therefore, only limited information is available about levels and fate of CPs in the environment. The few studies carried out so far report the presence of CPs in the aquatic and terrestrial environment and in sewage sludge^[2, 3]. Data from Europe are compiled in two risk assessment reports for short chain (SCCP)- and medium chain (MCCP) polychlorinated *n*-alkanes^[4, 5]. SCCPs have been most extensively used. They are toxic to aquatic invertebrates, persistent and do bioaccumulate^[2].

Consequently, several organizations and environmental agencies have imposed regulations on the application and/or environmental release of SCCPs. In particular, possible contamination of water by SCCPs is of concern. Therefore, the European Union included SCCPs in the list of priority hazardous substances in water policy directive 2000/60/EC^[6, 7]. It contains substances, which are persistent, toxic and bioaccumulate in food webs. Moreover, this measure requires the development of appropriate analytical methods for the investigation of environmental concentrations.

CPs were determined in sediments from the North and Baltic Sea during a sea-wide contamination monitoring in 2002. High resolution gas chromatography

(HRGC) combined with electron capture negative ionisation (ECNI) and low (LRMS) or high resolution mass spectrometry (HRMS) is normally employed for the determination of CP. Alternatively, a recently developed technique based on electron ionization (EI) tandem mass spectrometry (MS/MS) can be used for a first screening of CP levels in sediments^[8]. It allows the simultaneous determination of SCCPs and MCCPs (total CP concentration). Then, additional information about the congener and homologue patterns of selected samples can be obtained by HRGC-ECNI-LRMS.

Materials and Methods

Chemicals. SCCP (C₁₀₋₁₃, 55.5% Cl content) and MCCP (C₁₄₋₁₇, 57.0% Cl content) technical mixtures were purchased from Ehrenstorfer (Augsburg, Germany) as solutions in cyclohexane (concentration 100 ng/μl). [¹³C₁₀]-*trans*-chlordanes (Cambridge Isotope Laboratories, Mandover MA) and octachloronaphthalene OCN (Ehrenstorfer, Germany) were used as internal standards.

Sample clean-up. After addition of 10 ng of [¹³C₁₀]-*trans*-chlordanes and OCN in 10 μl of cyclohexane samples (particle size < 2 mm, dry weight 2-50 g depending on the total organic carbon content (TOC)) were Soxhlet extracted with 200 ml of n-hexane/CH₂Cl₂ (1:1, v/v) overnight. Elemental sulfur was removed with activated copper powder (230 mesh, Merck, Germany) during the Soxhlet extraction. Samples were purified with a column containing 16 g of Florisil[®] (1.5% water (w/w)). Fraction 1 was eluted with 60 ml of n-hexane plus 5 ml of CH₂Cl₂, fraction 2 with 55 ml of CH₂Cl₂. The latter contained the CPs. 10 ng of ε-HCH in 10 μl cyclohexane were added as recovery standard to the sediment extract before analysis. Quantification was based on a technical SCCP mixture with 55.5% and a MCCP mixture with 57.0% chlorine content as reference.

Sediment samples. Sediment samples were collected in the North and Baltic Sea (see Table 1) by the Federal Maritime and Hydrographic Agency (Hamburg, Germany) in August and September 2001 and 2002.

Table 1. Location, year of sampling and TOC content of sediment samples selected for CP analysis.

Sample	Location	TOC [%]	year
North Sea/German			
KS 8	54°02.00'N/8°12.50'E	0.34	2002
KS 11	54°04.00'N/8°07.50'E	1.67	2002
BL 2	54°14.00'N/8°22.50'E	0.57	2002
BL 4	54°30.00'N/7°48.00'E	0.21	2002
UE 18	54°30.00'N/7°60.00'E	< LOD*	2002
UE 28	54°45.00'N/8°12.00'E	0.1	2002
Baltic Sea			
715	54°02.90'N/10°50.00'	2.9	2001
718	54°18.90'N/11°33.10'	3.8	2001
710	54°25.10'N/10°13.30'	3.1	2001
710		5.28	2002
721	55°00.00'N/14°05.00'	5.18	2002

* limit of detection (0.1 %)

Instrumentation. Gas chromatographic separations were performed on a CP-3800 (Varian, USA) gas chromatograph equipped with a split/splitless injector and a fused silica capillary column (15 m, 0.25 mm i.d.) coated with 0.25 μ m DB5-MS (5% crosslinked phenyl-methylpolysiloxane, J&W Scientific, Folsom, USA). Splitless injections of 2.5 μ L volume were carried out at a injector temperature of 275 °C (Combi Pal autosampler, CTC Analytics, Zwingen, Switzerland). Helium was used as carrier gas at a constant flow of 2 mL/min. The temperature program was: 100 °C, isothermal for 1 min, then 50 °C/min to 300 °C, isothermal for 4 min.

A 1200 triple quadrupole MS (Varian, USA) was employed^[8]. Parameter in brief were: transfer line temperature 270 °C, ion source temperature 200 °C, manifold temperature 40 °C. EI-MS/MS spectra were recorded at 70 eV (emission current 300 μ A, dwell time 40 ms, resolution of Q1 at 0.8 u and of Q3 at 1.2 u and argon at 0.12-0.15 Pa). CP quantification was carried out with the collision induced dissociation (CID) m/z 91 \rightarrow 53, m/z 102 \rightarrow 65 and m/z 102 \rightarrow 67 (collision energy -10.0 V, -10.0 V or -18.0 V). The precursor ion m/z 383 [M-Cl]⁺ and the product ion m/z 276 [M-4Cl]⁺ were chosen for ¹³C₁₀-*trans*-chlordanes (collision energy -21.0 V). Recoveries and congener patterns were determined by HRGC-ECNI-LRMS as published elsewhere^[9].

Results and Discussion

Method validation. Recoveries of SCCPs and MCCPs were about 80% for spiked sediment samples (0.5-1.5 μg of technical CP mixture). The recovery of the internal standard OCN was between 80-90% and of [$^{13}\text{C}_{10}$]-*trans*-chlordane between 70-80%. Linearity was good for a concentration range between 0.5 and 100 $\text{ng}/\mu\text{L}$ technical SCCP mixture for all CIDs ($R^2 > 0.99$, 7-9 measuring points). Detection and quantification limits for a SCCP technical mixture with 55.5% chlorine content were in the range of 0.1-6 $\text{ng}/\mu\text{L}$ and 0.3-13 $\text{ng}/\mu\text{L}$ at a signal-to-noise ratio of 3:1 and 10:1, respectively, depending on the selected fragmentation.

Sediment samples. The total CP concentrations in sediments determined by EI-MS/MS (Table 2, average of all three CIDs) ranged between 5 and 499 ng/g of dry weight. Compared to published data of C_{10} - C_{20} chloroparaffin concentrations in North Sea sediments, the found concentrations were within the same order of magnitude^[10, 11].

Table 2. Total CP concentrations in sediments from the North and Baltic Sea given as dry weight and based on TOC content.

Sample	Total CP (ng/g)		Total CP ($\mu\text{g}/\text{g}$ TOC)	
	SCCP*	MCCP**	SCCP*	MCCP**
North Sea/German Bight				
KS 8	14	13	4.2	3.9
KS 11	112	146	6.7	8.7
BL 2	27	28	4.8	4.9
BL 4	8	9	3.7	4.3
UE 18	5	5	-	-
UE 28	9	9	9.1	8.6
Baltic Sea				
715	116	93	4.0	3.2
718	141	115	3.7	3.0
710 (2001)	262	211	8.4	6.8
710 (2002)	377	499	7.1	9.6
721/K 4	108	122	2.1	2.3

* Quantified with a SCCP mixture; ** quantified with a MCCP mixture.

There are small differences between the quantification with a SCCP or MCCP technical mixture with a similar chlorine content except for location 710. Except for KS 11 total CP concentrations in the North Sea (German Bight) were lower

than in the Baltic Sea. In general, the concentrations in the North Sea were too low for a determination of the congener and homologue pattern by ECNI-MS. However, total CP concentrations based on TOC content were in the same order of magnitude due to the high organic content in Baltic Sea sediments compared to the North Sea (Table 1). The highest total CP concentration in the North Sea based on TOC could be observed at location UE 28 with 0.1% TOC. The highest total CP concentration was found at KS 11. This location showed also high concentrations of hexachlorobenzene, polychlorinated biphenyls, DDT and hexachlorocyclohexanes in 1997 and 1998^[12]. KS 11 is situated in the Elbe estuary and therefore directly influenced by the Elbe. This higher total CP concentration is therefore not surprising. The highest total CP concentration in the Baltic Sea was found at location 710 (Kieler Förde). Sediment samples from location 715, 718 and 721 have similar CP concentrations. As a conclusion, Baltic Sea sediments are higher contaminated by CPs than the North Sea sediments. Up to now, the Baltic Sea belongs to the seas with one of the highest chlorinated hydrocarbon contamination about the world.^[12]

SCCPs and MCCPs were detected in sediments (Figure 1). Determination of homologue and congener pattern will follow by HRGC-ECNI-LRMS.

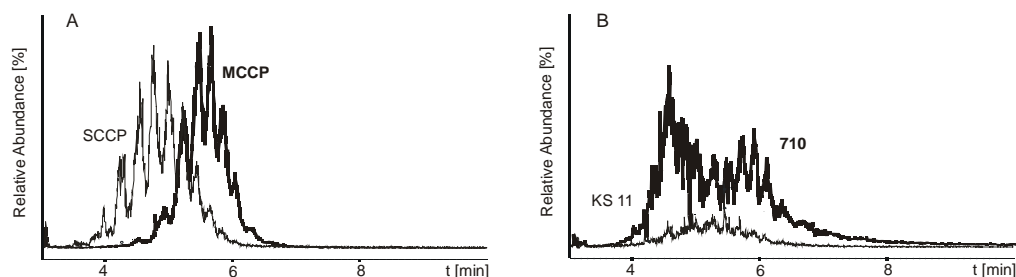


Figure 1: EI-MS/MS chromatograms of technical SCCP and MCCP mixture (A) and of Baltic and North Sea Sediments (B, location KS 11 and 710, 2002) using the CID m/z 102 \rightarrow 65.

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