

Congener group patterns of short and medium chain chloroparaffins in marine sediments

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Introduction

In 1990 the International Agency for Research of Cancer (IARC) classified short chain chloroparaffins (CPs) with 12 carbon atoms and a average chlorine of 60% as possibly carcinogenic to humans (group 2B).¹ No evidence was found for medium and long chain CPs. Based on this study, several organisations (OSPAR, HELCOM) and environmental agencies listed SCCPs as substances requiring special regulations. SCCPs were included on the list of priority hazardous substances in the field of water policy in the European Union.²

The analysis of CPs is difficult due to the large number of isomers (several thousands) and single capillary GC is insufficient for separation of all compounds. The presence of CPs in biota, air, water and sediments has been reported.³ There is limited information about CP levels in the German part of the North and Baltic Sea. 25-125 ng/g of C₁₀₋₂₄ were determined from mud flats at Kaiser Wilhelm Koog and Den Helder.⁴ Levels of C₁₀-C₂₀ chloroparaffins in North Sea sediments published as early as in 1980 were < 0.5-50 ng/g for 3 sediment locations.⁵

The aim of this work was to get an overview of SCCP and MCCP levels in the North and Baltic Sea. Information about concentrations, congener and homologue patterns of samples were obtained by high resolution gas chromatography (HRGC) combined with electron capture negative ionisation (ECNI) low resolution mass spectrometry (LRMS) using methane as reagent gas.

Materials and Methods

Chemicals. SCCP (C₁₀₋₁₃, 51.5, 55.5 and 63.0% Cl content) and MCCP (C₁₄₋₁₇, 47.0 and 57.0% Cl content) technical mixtures were purchased from Ehrenstorfer (Augsburg, Germany) as solutions in cyclohexane (concentration 100 ng/ml). [¹³C₁₀]-*trans*-chlordane (Cambridge Isotope Laboratories, Mandover MA) was used as internal standard (ISTD).

Sample clean-up. 10 g of dry sediment samples were extracted. Further details of the applied clean-up procedure are described in detail elsewhere.⁶ A further clean-up step was implemented in the procedure. Sample matrix not persistent to sulphuric acid was removed prior to the Florisil[®] clean-up by a column containing 1 g of water free sodium sulphate, 20 g of silica gel/sulfuric acid (44 %) and 1 g of sodium sulphate (glass column 20 cm long, 2.0 cm i.d.). The extract concentrated to 0.5 ml was placed on top of the column and the CP fraction was eluted with 70 ml of *n*-hexane/CH₂Cl₂ (1+1, v/v).

Instrumentation. Gas chromatographic separations were performed on a CP-3800 (Varian, Walnut Creek, 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 µm of crosslinked 5% phenyl-methylpolysiloxane (DB5-MS, J&W Scientific, Folsom, USA). Splitless injections (3 min) of 2.0 µL volume were carried out at an injector temperature of 275 °C (Combi Pal autosampler, CTC Analytics, Zwingen, Switzerland). Helium was used as carrier gas at a constant pressure of 68.9 kPa (10 psi). The temperature program was: 100 °C, isothermal for 2 min, then 10 °C/min to 260 °C, isothermal for 10 min.

A triple quadrupole MS (1200L, Varian, Walnut Creek, USA) was employed in the ECNI mode with methane as reagent gas at an ion source pressure of 7.3 mbar. The transfer line temperature was set at 280 °C, the ion source temperature at 200 °C and the manifold temperature at 40 °C. The mass spectrometer was tuned to optimal performance using PFTBA in the auto tune mode for both quadrupoles. SCCPs and MCCPs with 5-10 chlorine atoms were detected in the single ion monitoring mode using the two most abundant isotopes of the [M-Cl]⁻ cluster for each CP compound (dwell time 0.250 s per cycle) and m/z 419.8 for the internal standard.

Results and Discussion

Method validation. Recovery of the ISTD was between 56-81% for the sediment samples and comparable to spiked sediment samples.⁶ Linearity was good for a concentration range between 1 and 100 ng/µL technical SCCP and MCCP mixture (R² >0.99, 7-9 measuring points). The limit of detection (LOD) for the compounds C₁₁H₁₆Cl₆ and C₁₂H₁₈Cl₆ was < 1 ng/µl in a technical SCCP mixture at a signal-to-noise ratio of 3:1, and the limit of quantification (LOQ) was 2.1 and 2.5 ng/µl at a signal-to-noise ratio of 10:1. The LODs for C₁₄H₂₃Cl₇ and C₁₅H₂₅Cl₇ were 0.2 and 0.5 ng/µl and the LOQs 0.8 and 1.7 ng/µl in a technical MCCP mixture.

Removal of interfering compounds. The applied Florisil® column was efficient for the removal of toxaphenes, DDT-compounds, PCB and heptachlor as the test with model compounds demonstrated. These substances eluted completely in the first fraction. *a*-HCH, *cis/trans*-chlordane and *cis*-nonachlor coelute with CPs in the second fraction of the Florisil® column. *trans*-Nonachlor was found in both fractions.

Quantification. The quantification of the CPs was performed according to the method described by Reth et al. (2004). SCCPs and MCCPs could be detected in all samples. Concentrations are summarized in table 1. The SCCP concentrations ranged between 8-63 ng/g dry weight (d.w.). MCCP concentrations between 22 and 140 ng/g d.w. were determined. The results were in good agreement with earlier published results worldwide (SCCP in river sediments: 4.5-80.8 ng/g d.w. in the Czech Republic⁸, 0.25-3.26 µg/g in Spain⁹ and a average of 49 ng/g d.w. for Lake Ontario sediments¹⁰). Kemmlin et al. (2002) reported MCCP concentrations between 1.1 and 16.4 µg/g for marine sediments influenced by a CP manufacturer in Australia.¹¹ In 1994 MCCP concentrations of <10-370 ng/g were determined in German river sediments and 5 ng/g (C₁₄₋₁₈) in surface sediment from Lake Zürich.¹²

MCCP concentrations were highest in all 11 samples (ratio MCCP/SCCP 1.1-3.2, Table 1). Similar observations were also made for German and Swiss river and lake sediments.¹¹ There, MCCP levels were 2 to 10 times higher. Reasons could be the higher production/consumption of MCCPs in Europe or a preferred adsorption of MCCP. The use of SCCPs decreased from 13,000 tonnes in 1994 to 4,000 tonnes in 1998 for the European Union.¹³ The production of MCCPs is still high within the EU (45,000-160,000 tonnes/year).¹⁴

Congener profiles of sediment samples. Do- and tridecanes with 5-7 and tetradecanes with 6-8 chlorine atoms were the main CP congeners in sediment samples (Table 1). Higher contents of C₁₂ and C₁₃ compounds were determined in samples from Australia.¹¹ Surface sediments from Lake Ontario harbors also showed higher abundances of C₁₂ and C₁₃ compounds (42-81% of the relative abundance, 8 samples).¹³ Higher relative abundances of C₁₃ compounds characterized sediments influenced by local industrial sources.¹⁰ Štejnarová et al. (2005) reported samples dominated by undecanes from 3 different areas in the Czech Republic. The degree of chlorination was calculated to 60-70% for SCCPs and was higher than for sediments from the North and Baltic Sea (59-61%, Table 1).

3 of 4 sediment samples from Australia showed higher relative abundances for C₁₅ (37-41%) compounds than C₁₄.¹¹ C₁₆₋₁₇ congeners were also detected. Sediment samples from the North and Baltic Sea showed a congener pattern similar to the quantification standard with a higher relative abundance of C₁₄ (Table 1). C₁₆ and C₁₇ were not determined. Except one sediment sample from Canada no further MCCP congener profiles determined by HRGC-ECNI-LRMS were found in the literature.¹⁵

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Table 1. Comparison of the calculated average chlorine content [% Cl], the average molar mass [g/mol], main components, distribution of SCCP and MCCP congeners [%] and concentrations [ng/g dry weight] in samples from North and Baltic Sea.

EMV - General – Environmental Levels

Sample (year)	Location	% Cl		Molar mass [g/mol]		Main component		Relative Distribution [%]						Concentration [ng/g]	
		SCCP	MCCP	SCCP	MCCP	SCCP	MCCP	C ₁₀	C ₁₁	C ₁₂	C ₁₃	C ₁₄	C ₁₅	SCCP*	MCCP*
North Sea															
1 (May, 2003)	54° 02.00'N/8° 12.50' E	60	56	417	452	C ₁₃ Cl ₆	C ₁₄ Cl _{7/8}	9	19	22	50	62	38	27	87
1 (May, 2004)		60	56	404	453	C ₁₁ Cl ₇	C ₁₄ Cl _{7/8}	11	30	30	29	59	40	43	48
2 (May, 2003)	54° 04.00'N/8° 07.50' E	61	57	424	455	C ₁₃ Cl ₇	C ₁₄ Cl _{7/8}	8	18	34	40	63	37	13	34
2 (May, 2004)		61	56	418	455	C ₁₃ Cl ₇	C ₁₄ Cl _{6/7}	7	23	32	39	55	44	63	149
Baltic Sea															
3 (June 2004)	54° 25.10'N/10° 13.30' E	59	56	395	452	C ₁₃ Cl ₆	C ₁₄ Cl _{6/7}	12	34	22	32	61	40	15	23
4 (June 2004)	54° 02.90'N/10° 50.00' E	61	57	410	454	C ₁₂ Cl ₇	C ₁₄ Cl _{6/7}	13	32	29	25	58	41	22	43
5 (June 2004)	54° 18.90'N/11° 33.10' E	60	56	403	451	C ₁₃ Cl ₆	C ₁₄ Cl _{6/7}	14	30	25	31	68	31	53	85
6 (June 2004)	55° 00.00'N/14° 05.00' E	60	57	414	452	C ₁₃ Cl ₇	C ₁₄ Cl _{7/8}	12	22	25	42	67	33	27	72
7 (June 2004)	54° 28.00'N/9° 52.00' E	61	57	415	455	C ₁₂ Cl _{5/6}	C ₁₄ Cl _{7/8}	8	22	48	22	64	35	31	39
8 (June 2004)	54° 08.00'N/14° 10.00' E	60	56	407	453	C ₁₃ Cl ₇	C ₁₄ Cl _{6/7}	16	23	24	37	55	45	8	22
9 (June 2004)	54° 11.20'N/13° 46.00' E	61	57	419	459	C ₁₃ Cl ₇	C ₁₄ Cl _{7/8}	6	19	41	34	63	36	26	33
Quantification standard**															
SCCP (51.5% Cl)		58±0.2		384±3.6		C ₁₂ Cl _{6/7}		5±0.7	28±1.9	38±0.5	30±2.4				
SCCP (55.5% Cl)		59±0.1		396±1.9		C ₁₂ Cl _{6/7}		6±0.7	32±2.6	38±1.8	24±3.0				
SCCP (63% Cl)		63±0.1		432±1.6		C ₁₁ Cl _{7/8}		7±1.0	35±2.2	34±2.1	24±1.4				
MCCP (47 % Cl)			52±0.3		412±3.5		C ₁₄ Cl _{6/7}					69±4.4	31±4.4		
MCCP (57 % Cl)			58±0.3		466±3.9		C ₁₄ Cl _{7/8}					73±2.4	27±2.4		
* quantification according to Reth et al. (2004) ⁷															
** 3 measurements on different days and 2 on each day															