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Limitations of low resolution mass spectrometry in the electron capture negative ionization mode for the analysis of short- and medium-chain chlorinated paraffins

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Abstract The analysis of complex mixtures of chlorinated paraffins (CPs) with short (SCCPs, C_{10} – C_{13}) and medium (MCCPs, C_{14} – C_{17}) chain lengths can be disturbed by mass overlap, if low resolution mass spectrometry (LRMS) in the electron capture negative ionization mode is employed. This is caused by CP congeners with the same nominal mass, but with five carbon atoms more and two chlorine atoms less; for example $C_{11}H_{17}^{37}Cl^{35}Cl_6$ (m/z 395.9) and $C_{16}H_{29}^{35}Cl_5$ (m/z 396.1). This can lead to an overestimation of congener group quantity and/or of total CP concentration. The magnitude of this interference was studied by evaluating the change after mixing a SCCP standard and a MCCP standard 1+1 (S+MCCP mixture) and comparing it to the single standards. A quantification of the less abundant C_{16} and C_{17} congeners present in the MCCP standard was not possible due to interference from the major C_{11} and C_{12} congeners in the SCCPs. Also, signals for SCCPs (C_{10} – C_{12}) with nine and ten chlorine atoms were mimicked by MCCPs (C_{15} – C_{17}) with seven and eight chlorine atoms (for instance $C_{10}H_{12}Cl_{10}$ by $C_{15}H_{24}Cl_8$). A similar observation was made for signals from C_{15} – C_{17} CPs with four and five chlorine atoms resulting from SCCPs (C_{10} – C_{12}) with six and seven chlorine atoms (such as $C_{15}H_{28}Cl_4$ by $C_{10}H_{16}Cl_6$) in the S+MCCP mixture. It could be shown that the quantification of the most abundant congeners (C_{11} – C_{14}) is not affected by any interference. The determination of C_{10} and C_{15} congeners is partly disturbed, but this can be detected by investigating isotope ratios, retention time ranges and the shapes of the CP signals. Also, lower chlorinated compounds forming $[M+Cl]^-$ as the most abundant ion instead of $[M-Cl]^-$ are especially sensitive to systematic errors caused by superposition of ions of different composition and the same nominal mass.

Keywords Polychlorinated *n*-alkanes · Chlorinated paraffins · ECNI low resolution mass spectrometry · Self-interferences

Introduction

Commercially produced chlorinated paraffins (CPs) are classified according to their carbon chain length into short chain CPs (SCCPs, C_{10} – C_{13}), medium chain CPs (MCCPs, C_{14} – C_{17}) and long chain CPs (LCCPs, $>C_{17}$). The chlorine content of these mixtures can vary from 30–70% depending on their application [1]. Technical CPs are mainly used as extreme pressure additives in lubricants and cutting oils as well as plasticizers and fire retardants. They have also found application as replacements for other persistent polychlorinated chemicals, such as polychlorinated biphenyls [2]. CPs are classified as persistent and non-biodegradable, and they accumulate in the food chain [3]. Though the global production of SCCPs has been reduced since the early 1980s [2], the overall annual production is still in the range of 380,000 tons [4]. Global redistribution by long-range atmospheric transport is suggested as the reason for the ubiquitous occurrence of CPs in the environment, including in remote areas such as the Canadian Arctic [5]. SCCPs are of particular interest due to the high amounts released into the environment, and due to them having the highest toxicity of all CP products [2].

The quantification of CPs is a demanding task. Although the levels of CPs were determined in environmental samples in the 1980s [6], as yet only very limited information has been published about the levels and fate of short- and medium-chain CPs in the environment [1]. This is mainly due to the extreme complexity of CP mixtures containing thousands of different isomers, enantiomers and diastereomers. Currently, no gas chromatographic technique is able to separate CPs partly or completely into single isomers [7].

CP analysis is mainly carried out by high resolution gas chromatography (HRGC) coupled to high resolution (HR) mass spectrometry (MS) in the electron capture neg-

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ative ionization (ECNI) mode. This is a very selective detection method, which eliminates interferences by other polychlorinated pollutants and by CPs with the same nominal mass [7]. However, this detection method is not available at many laboratories and is too costly for routine analysis.

Therefore, low resolution (LR) MS is also used for the quantification of CPs. An international intercomparison of methods for SCCP analysis showed that LRMS and HRMS can give comparable quantitative results [8]. Indeed, published levels of CPs in biota were similar when quantified by LRMS and HRMS [7, 9]. Nevertheless, the use of LRMS instead of HRMS increases the risk of interference, which has to be controlled and eliminated, if possible. An improved sample clean-up, removing other interfering polychlorinated compounds, is one possibility [10]. However, disturbances might also occur between molecular ions and fragments of CPs with the same nominal mass, if mixtures of SCCPs and MCCPs are present. This can result in an overestimation of the total PCA concentration.

This work investigates the risk from systematic errors due to mass interferences between SCCPs and MCCPs when using LRMS in the ECNI mode. Ways to minimize disturbances will be discussed in detail too, such as the careful selection of congener masses and retention time ranges, or by checking signal shapes and isotope ratios. It will be demonstrated that a simultaneous quantification of SCCPs and MCCPs and their differentiation in environmental samples is also possible by LRMS.

Experimental

Chemicals and solvents

Cyclohexane for pesticide residue analysis was purchased from Scharlau (Barcelona, Spain). Technical SCCPs (C_{10-13} , 55.5% chlorine, 100 ng/ μ l, solution in cyclohexane) and technical MCCPs (C_{14-17} , 52% chlorine, 100 ng/ μ l, solution in cyclohexane) as well as ϵ -hexachlorocyclohexane (ϵ -HCH, 10 ng/ μ l, solution in cyclohexane, purity 99.9%) were obtained from Ehrenstorfer (Augsburg, Germany). Solutions for analysis contained 25 ng/ μ l of the respective CP mixture and 50 pg/ μ l of ϵ -HCH.

Instrumentation

Chromatographic separations were carried out on an HP 5890II (Hewlett Packard, Palo Alto, USA) gas chromatograph equipped with a split/splitless injector and a fused silica capillary column (15 m, 0.25 mm i.d.) coated with a 0.25 μ m-thick film of DB-5MS (crosslinked 5%-phenyl-95%-methylpolysiloxane, J&W Scientific, Folsom, USA). Sample volumes of 2 μ l were injected in the splitless mode (splitless time 2 min) at an injector temperature of 275 °C. Helium (99.999%, Carbagas, Basel, Switzerland) was used as carrier gas at a column inlet 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.

An HP 5989B mass spectrometer (Hewlett Packard, Palo Alto, USA) was employed in the electron capture negative ionization (ECNI) mode using methane (99.995%, Carbagas, Basel, Switzerland) as reagent gas at a pressure of 1.0–1.6 mbar (0.8–1.2 Torr). The mass spectrometer was tuned to optimal performance using perfluorotributylamine at m/z 283, 414 and 452. The electron energy was set to 100 eV. The ion source temperature was 200 °C,

the quadrupole temperature 100 °C, and the transfer line temperature 280 °C. Compounds were detected in the selected ion monitoring (SIM) mode at a dwell time of 100 ms per ion using the two most abundant $[M-Cl]^-$ isotope ions of each CP congener (see Table 1) and m/z 254.9 for the internal standard ϵ -HCH.

Results and discussion

Studies of the composition of CP mixtures and congener-specific analyses of environmental samples are scarce due to the complexity of CP mixtures. HRMS at a resolution of 12,000 is often used to exclude interferences from CP fragments with the same nominal mass as the $[M-Cl]^-$ ions or from other organic pollutants not removed by the applied clean-up procedure [7]. As shown below, LRMS (~1000 resolving power) requires more detailed knowledge about possible interferences to enable the correct determination of CP compositions.

Congeners with similar nominal masses

Technical CPs contain thousands of isomers with the general elemental composition $C_nH_{2n+2-x}Cl_x$, resulting in some overlap of the chlorine isotope pattern of different CP congeners. Table 1 summarizes the mass-to-charge ratios of the two most abundant isotope signals of each congener normally used for quantification and identification of CPs [7]. It demonstrates that congeners with five carbon atoms more and two chlorine atoms less have a nearly identical nominal mass-to-charge ratio, which cannot be resolved by LRMS.

Influence of mass overlap on CP composition

A SCCP standard, a MCCP standard and a 1+1 mixture of both were used to study the influence of mass overlap on composition, at first ignoring correct isotope ratios and retention time ranges. The observed homologue and congener patterns of all three are given in Fig. 1. The SCCP mixture contained mainly congeners with C_{11} and C_{12} chains (relative contribution of ΣC_{11} 33%, of ΣC_{12} 38%). C_{10} and C_{13} congeners represented 8 and 21%, respectively. The MCCP mixture consisted mainly of C_{14} congeners (ΣC_{14} 75%, ΣC_{15} 21%, ΣC_{16} 2%, ΣC_{17} 2%).

Figure 1A shows that the presence of C_{15} and especially C_{16} , as well as C_{17} congeners in the SCCP mixture, is mimicked by masses with similar mass-to-charge ratios originating from C_{10} , C_{11} and C_{12} congeners with correspondingly five carbon atoms less and two chlorine atoms more (see Table 1 for details). C_{16} and C_{17} congeners cannot be quantified by LRMS, if C_{11} and C_{12} are major components in an environmental sample. Furthermore, a small amount of C_9 (2%) and C_{14} (1.5%) congeners were detected in the SCCP mixture.

On the other hand, C_{16} and C_{17} congeners are minor components in the MCCP mixture (see Fig. 1B) and do not therefore affect the quantification of the higher chlori-

Table 1 Mass-to-charge ratios of the $[M-Cl]^-$ ions (abbreviated to X in the table) of the two most abundant isotopes of SCCP and MCCP congeners used for quantification and identification

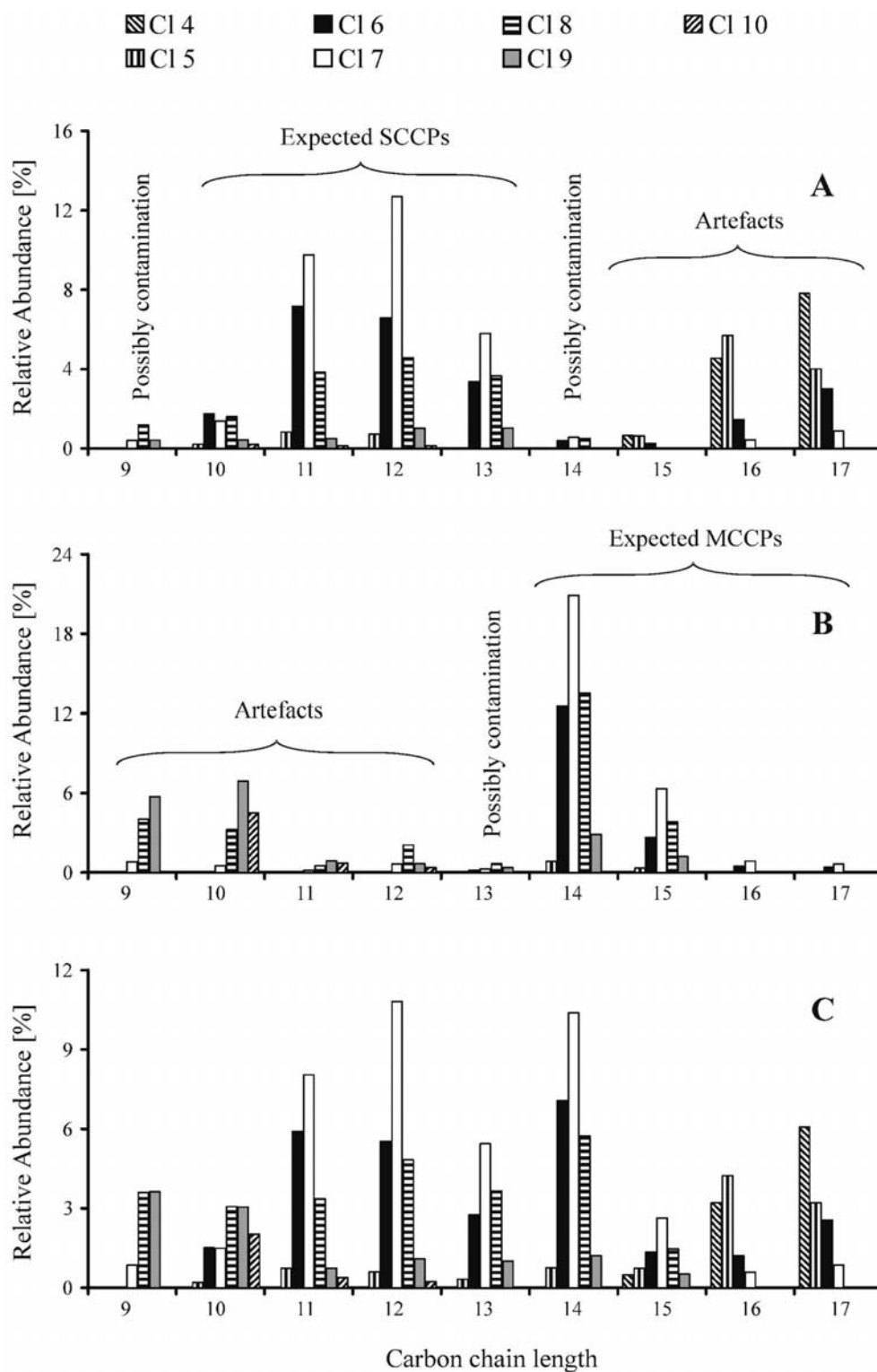
Short chain CPs			Medium chain CPs		
CP congener	Most abundant isotope (100%)	Second abundant isotope	CP congener	Most abundant isotope (100%)	Second abundant isotope
C ₉ H ₁₄ Cl ₆	298.9 (X+2)	300.9 (X+4, 64%)	C ₁₄ H ₂₆ Cl ₄	299.1 (X)	301.1 (X+2, 96%)
C ₉ H ₁₃ Cl ₇	332.9 (X+2)	334.9 (X+4, 80%)	C ₁₄ H ₂₅ Cl ₅	335.1 (X+2)	333.1 (X, 78%)
C ₉ H ₁₂ Cl ₈	366.9 (X+2)	368.9 (X+4, 96%)	C ₁₄ H ₂₄ Cl ₆	369.0 (X+2)	371.0 (X+4, 64%)
C ₉ H ₁₁ Cl ₉	402.8 (X+4)	400.8 (X+2, 89%)	C ₁₄ H ₂₃ Cl ₇	403.0 (X+2)	405.0 (X+4, 80%)
			C ₁₄ H ₂₂ Cl ₈	436.9 (X+2)	438.9 (X+4, 96%)
			C ₁₄ H ₂₁ Cl ₉	472.9 (X+4)	470.9 (X+2, 89%)
			C ₁₄ H ₂₀ Cl ₁₀	506.9 (X+4)	504.9 (X+2, 78%)
C ₁₀ H ₁₈ Cl ₄	243.1 (X)	245.1 (X+2, 96%)			
C ₁₀ H ₁₇ Cl ₅	279.0 (X+2)	277.0 (X, 78%)			
C ₁₀ H ₁₆ Cl ₆	312.9 (X+2)	314.9 (X+4, 64%) 64%	C ₁₅ H ₂₈ Cl ₄	313.1 (X)	315.1 (X+2, 96%)
C ₁₀ H ₁₅ Cl ₇	346.9 (X+2)	348.9 (X+4, 80%)	C ₁₅ H ₂₇ Cl ₅	349.1 (X+2)	347.1 (X, 78%)
C ₁₀ H ₁₄ Cl ₈	380.9 (X+2)	382.9 (X+4, 96%)	C ₁₅ H ₂₆ Cl ₆	383.0 (X+2)	385.0 (X+4, 64%)
C ₁₀ H ₁₃ Cl ₉	416.8 (X+4)	414.8 (X+2, 89%)	C ₁₅ H ₂₅ Cl ₇	417.0 (X+2)	419.0 (X+4, 80%)
C ₁₀ H ₁₂ Cl ₁₀	450.8 (X+4)	448.8 (X+2, 78%)	C ₁₅ H ₂₄ Cl ₈	451.0 (X+2)	453.0 (X+4, 96%)
			C ₁₅ H ₂₃ Cl ₉	486.9 (X+4)	484.9 (X+2, 89%)
			C ₁₅ H ₂₂ Cl ₁₀	520.9 (X+4)	518.9 (X+2, 78%)
C ₁₁ H ₂₀ Cl ₄	257.1 (X)	259.1 (X+2, 96%)			
C ₁₁ H ₁₉ Cl ₅	293.0 (X+2)	291.0 (X, 78%)			
C ₁₁ H ₁₈ Cl ₆	327.0 (X+2)	329.0 (X+4, 64%)	C ₁₆ H ₃₀ Cl ₄	327.1 (X)	329.1 (X+2, 96%)
C ₁₁ H ₁₇ Cl ₇	360.9 (X+2)	362.9 (X+4, 80%)	C ₁₆ H ₂₉ Cl ₅	363.1 (X+2)	361.1 (X, 78%)
C ₁₁ H ₁₆ Cl ₈	394.9 (X+2)	396.9 (X+4, 96%)	C ₁₆ H ₂₈ Cl ₆	397.0 (X+2)	399.0 (X+4, 64%)
C ₁₁ H ₁₅ Cl ₉	430.9 (X+4)	428.9 (X+2, 89%)	C ₁₆ H ₂₇ Cl ₇	431.0 (X+2)	433.0 (X+4, 80%)
C ₁₁ H ₁₄ Cl ₁₀	464.8 (X+4)	462.8 (X+2, 78%)	C ₁₆ H ₂₆ Cl ₈	465.0 (X+2)	467.0 (X+4, 96%)
			C ₁₆ H ₂₅ Cl ₉	500.9 (X+4)	498.9 (X+2, 89%)
			C ₁₆ H ₂₄ Cl ₁₀	534.9 (X+4)	532.9 (X+2, 78%)
C ₁₂ H ₂₂ Cl ₄	271.1 (X)	273.1 (X+2, 96%)			
C ₁₂ H ₂₁ Cl ₅	307.0 (X+2)	305.1 (X, 78%)			
C ₁₂ H ₂₀ Cl ₆	341.0 (X+2)	343.0 (X+4, 64%)	C ₁₇ H ₃₂ Cl ₄	341.1 (X)	343.1 (X+2, 96%)
C ₁₂ H ₁₉ Cl ₇	374.9 (X+2)	376.9 (X+4, 80%)	C ₁₇ H ₃₁ Cl ₅	377.1 (X+2)	375.1 (X, 78%)
C ₁₂ H ₁₈ Cl ₈	408.9 (X+2)	410.9 (X+4, 96%)	C ₁₇ H ₃₀ Cl ₆	411.1 (X+2)	413.1 (X+4, 64%)
C ₁₂ H ₁₇ Cl ₉	444.9 (X+4)	442.9 (X+2, 89%)	C ₁₇ H ₂₉ Cl ₇	445.0 (X+2)	447.0 (X+4, 80%)
C ₁₂ H ₁₆ Cl ₁₀	478.8 (X+4)	476.8 (X+2, 78%)	C ₁₇ H ₂₈ Cl ₈	479.0 (X+2)	481.0 (X+4, 96%)
			C ₁₇ H ₂₇ Cl ₉	514.9 (X+4)	512.9 (X+2, 89%)
			C ₁₇ H ₂₆ Cl ₁₀	548.9 (X+4)	546.9 (X+2, 78%)
C ₁₃ H ₂₄ Cl ₄	285.1 (X)	287.1 (X+2, 96%)			
C ₁₃ H ₂₃ Cl ₅	321.1 (X+2)	319.1 (X, 78%)			
C ₁₃ H ₂₂ Cl ₆	355.0 (X+2)	357.0 (X+4, 64%)			
C ₁₃ H ₂₁ Cl ₇	389.0 (X+2)	391.0 (X+4, 80%)			
C ₁₃ H ₂₀ Cl ₈	422.9 (X+2)	424.9 (X+4, 96%)			
C ₁₃ H ₁₉ Cl ₉	458.9 (X+4)	456.9 (X+2, 89%)			
C ₁₃ H ₁₈ Cl ₁₀	492.9 (X+4)	490.9 (X+2, 78%)			

nated C₁₁ and C₁₂ congeners with corresponding mass. C₁₆ and C₁₇ congeners contribute less than 4% to the overall quantity of C₁₁ and C₁₂ congeners present in the 1+1 mixture. This is in agreement with published C₁₆+C₁₇ contents of ≤7% in technical CPs and environmental samples [11]. Therefore, the systematic error by interference for C₁₁ and C₁₂ congeners is comparable to the quantification uncertainty. Trace amounts (<2%) of C₁₃ congeners were present in the MCCP mixture. The C₉ (11%) and C₁₀ (7%) congeners apparently present were mimicked by C₁₄ and C₁₅ congeners with similar mass-to-charge ratios (see Table 1). C₉ congeners are usually not determined in envi-

ronmental samples, whereas the amount of C₁₀ congeners could be overestimated.

Figure 1C shows the resulting change of pattern for a 1+1 mixture of SCCPs and MCCPs due to the interferences described above. The presence of C₁₁ and C₁₂ congeners led to a 3–25-fold overestimation of the concentrations of C₁₆ and C₁₇ congeners. The C₁₅–C₁₇ congeners with four and five chlorine atoms (25%) apparently present were mimicked by the respective short chain congeners (C₁₀–C₁₂) with six and seven chlorine atoms (such as C₁₅H₂₈Cl₄ and C₁₀H₁₆Cl₆). In addition, traces (<1%) of C₁₀–C₁₂ congeners with nine and ten chlorine atoms were

Fig. 1 Homologue and congener pattern (C_9 – C_{17}) of a SCCP standard (A), a MCCP standard (B) and a mixture (1+1) of a SCCP and MCCP standard (C), as determined by HRGC-ECNI-LRMS



mainly simulated by the respective medium chain congeners (C_{15} – C_{17}) with seven and eight chlorine atoms (for example $C_{10}H_{12}Cl_{10}$ and $C_{15}H_{24}Cl_8$). Multiple HCl elimination, as reported by Coelhan [9], can also lead to corresponding interferences, but was not observed in this work, possibly due to other ion source conditions.

Identification of interferences by isotope ratios

One way to detect possible interferences due to co-eluting CPs is to control the chlorine isotope ratio. Here, the signal area of the most abundant $[M-Cl]^-$ isotope was divided by that of the second most abundant $[M-Cl]^-$ isotope, and this ratio was employed. A significant deviation (>0.10)

Table 2 Selected isotope ratios (higher mass divided by lower mass) of the signal area of the two most abundant isotopes of the $[M-Cl]^-$ ions (see Table 1) determined in a SCCP standard, a MCCP standard and in a 1+1 mixture. Allocations of origin are given for the latter. Isotope ratios have a precision of 0.10

CP congener	Isotope ratios			Possible origin of the signal in the S+MCCP mixture
	SCCP	MCCP	S+MCCP	
C ₁₀ H ₁₈ Cl ₄	–	–	–	–
C ₁₀ H ₁₇ Cl ₅	1.00	–	1.18	SCCP
C ₁₀ H ₁₆ Cl ₆	1.60	–	1.58	SCCP
C ₁₀ H ₁₅ Cl ₇	1.45	2.07	1.39	SCCP
C ₁₀ H ₁₄ Cl ₈	2.65	1.30	1.55	^a
C ₁₀ H ₁₃ Cl ₉	0.34	1.59	1.12	^a
C ₁₀ H ₁₂ Cl ₁₀	0.63	1.85	1.64	^a
C ₁₁ H ₂₀ Cl ₄	–	–	–	–
C ₁₁ H ₁₉ Cl ₅	0.96	–	0.90	SCCP
C ₁₁ H ₁₈ Cl ₆	1.63	–	1.59	SCCP
C ₁₁ H ₁₇ Cl ₇	1.28	0.41	1.26	SCCP
C ₁₁ H ₁₆ Cl ₈	1.20	1.00	1.23	SCCP
C ₁₁ H ₁₅ Cl ₉	0.48	1.48	0.67	^a
C ₁₁ H ₁₄ Cl ₁₀	0.44	2.12	0.89	^a
C ₁₂ H ₂₂ Cl ₄	–	–	–	–
C ₁₂ H ₂₁ Cl ₅	0.87	–	0.85	SCCP
C ₁₂ H ₂₀ Cl ₆	1.64	–	1.64	SCCP
C ₁₂ H ₁₉ Cl ₇	1.27	1.62	1.31	SCCP
C ₁₂ H ₁₈ Cl ₈	1.07	4.54	1.23	SCCP
C ₁₂ H ₁₇ Cl ₉	1.01	0.26	0.57	^a
C ₁₂ H ₁₆ Cl ₁₀	0.96	0.35	0.43	MCCP
C ₁₃ H ₂₄ Cl ₄	–	–	–	–
C ₁₃ H ₂₃ Cl ₅	0.85	–	0.86	SCCP
C ₁₃ H ₂₂ Cl ₆	1.52	1.82	1.47	SCCP
C ₁₃ H ₂₁ Cl ₇	1.30	1.47	1.31	SCCP
C ₁₃ H ₂₀ Cl ₈	1.02	3.16	1.10	SCCP
C ₁₃ H ₁₉ Cl ₉	1.08	0.23	0.84	^a
C ₁₄ H ₂₆ Cl ₄	–	–	–	–
C ₁₄ H ₂₅ Cl ₅	–	0.75	0.78	MCCP
C ₁₄ H ₂₄ Cl ₆	0.54	1.74	1.56	MCCP
C ₁₄ H ₂₃ Cl ₇	1.19	1.30	1.29	MCCP
C ₁₄ H ₂₂ Cl ₈	0.63	1.07	1.06	MCCP
C ₁₄ H ₂₁ Cl ₉	–	1.09	1.13	MCCP
C ₁₅ H ₂₈ Cl ₄	1.56	–	1.52	SCCP
C ₁₅ H ₂₇ Cl ₅	0.74	0.91	0.75	SCCP
C ₁₅ H ₂₆ Cl ₆	0.60	1.87	1.32	^a
C ₁₅ H ₂₅ Cl ₇	–	1.33	1.27	MCCP
C ₁₅ H ₂₄ Cl ₈	–	1.07	1.09	MCCP
C ₁₅ H ₂₃ Cl ₉	–	1.11	1.23	MCCP
C ₁₆ H ₃₀ Cl ₄	1.69	–	1.60	SCCP
C ₁₆ H ₂₉ Cl ₅	0.59	–	0.60	SCCP
C ₁₇ H ₃₂ Cl ₄	1.63	–	1.68	SCCP
C ₁₇ H ₃₁ Cl ₅	0.76	–	0.74	SCCP

^a Identification was not possible

should be observable as long as the number of chlorine atoms in the overlapping mass signal is different. Isotope ratios of the respective congeners groups were determined in the SCCP and the MCCP standard as well as in their 1+1 mixture. Isotope ratios and their origin or eventual disturbance are listed in Table 2.

The isotope ratios allowed to identify the origin of the CP signal for the following CPs: C₁₀ with 5–7 chlorine atoms, C₁₁, C₁₂ and C₁₃ with 5–8 chlorine atoms, C₁₄ with 5–9 chlorine atoms and C₁₅ with 7–9 chlorine atoms (see Table 2). A disturbance was observed in eight of overall 43 isotope ratios.

As mentioned before, masses similar to medium chain congeners (C₁₅–C₁₇) with four and five chlorine atoms can originate from the respective short chain congeners (C₁₀–C₁₂) with six and seven chlorine atoms. This was also confirmed by the isotope ratios of these congeners. They were identical for C₁₅H₂₈Cl₄, C₁₆H₃₀Cl₄, C₁₇H₃₂Cl₄ and C₁₅H₂₇Cl₅, C₁₆H₂₉Cl₅ and C₁₇H₃₁Cl₅ in the 1+1 mixture and in the SCCP standard (see Table 2).

The two most abundant $[M-Cl]^-$ isotopes of higher chlorinated short chain congeners (7–9 chlorine atoms) overlap with those from compounds with two carbon atoms more and one chlorine atom less (for instance C₁₂H₁₇³⁷Cl₂³⁵Cl₇ by C₁₄H₂₂³⁷Cl₅³⁵Cl₃, see Table 3). Tomy et al. [7] also remarked upon this. The isotope ratios of short chain congeners (C₁₀–C₁₃) with nine or ten chlorine atoms were in the 1+1 mixture between those of the SCCP and MCCP standard and did not allow any allocation.

Control of retention times

CP congeners cannot be identified by retention time due to insufficient separation by HRGC. However, the retention time range of congener groups varies sufficiently to differentiate between SCCPs and MCCPs in many cases. Combining this information with the isotope ratios helps to determine whether a group of congeners in a sample originates from SCCPs, MCCPs or from both.

The mass chromatograms of the most abundant isotope signals of the elemental compositions of C₁₀H₁₄Cl₈ and C₁₅H₂₆Cl₆ are shown in Fig. 2 for a SCCP and a MCCP standard, and a mixture of both. These elemental compositions have the same nominal mass but different isotope ratios. Moreover, retention time ranges and overall signal shapes deviate. C₁₀H₁₄Cl₈ congeners eluted between 14–18 min for the SCCP mixture, and C₁₅H₂₆Cl₆ congeners between 16–20 min for the MCCP mixture. The shapes of the chromatographic signals were influenced by both the selected mass and the origin (s or m) of the CPs. In the S+MCCP mixture, the shape and the retention time range of the respective chromatographic signals, as well as the isotope ratios, deviated from those of the single CP standards due to the interferences between C₁₀H₁₄Cl₈ and C₁₅H₂₆Cl₆. For quantification, a selection of a retention time window for the main elution range of a congener group would allow us to improve selectivity somewhat, although at the risk of introducing a systematic error due to the cut-off of minor humps.

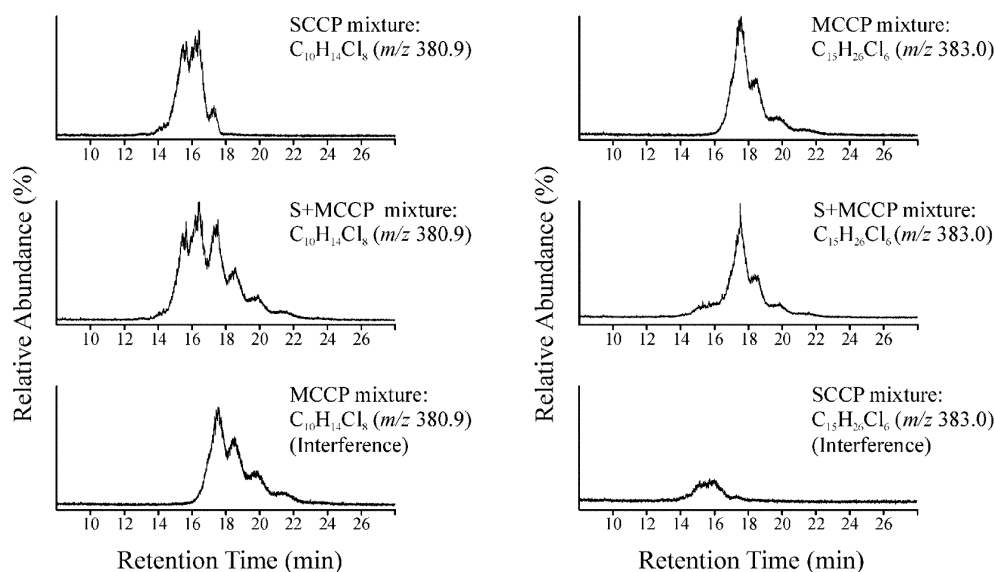
Formation of $[M+Cl]^-$

The ECNI mass spectra of CPs contain the three main ions $[M-HCl]^-$, $[M-Cl]^-$ and $[M+Cl]^-$ with a structure-de-

Table 3 Mass-to-charge ratios of $[M-Cl]^-$ ions (assigned as X in the table) of the most abundant isotopes of higher chlorinated short chain congeners, and the corresponding overlap with X+8 and X+10 isotopes of CP isomers with two carbons more and one chlorine less

Short chain CPs			Overlapping CP congener		
CP congener	Most abundant isotope (100%)	Second abundant isotope	CP congener	X+8 isotope	X+10 isotope
$C_{10}H_{15}Cl_7$	346.9 (X+2)	348.9 (X+4, 80%)	$C_{12}H_{20}Cl_6$	347.0 (3.3%)	349.0 (0.2%)
$C_{10}H_{14}Cl_8$	380.9 (X+2)	382.9 (X+4, 96%)	$C_{12}H_{19}Cl_7$	380.9 (8.2%)	382.9 (1.0%)
$C_{10}H_{13}Cl_9$	416.8 (X+4)	414.8 (X+2, 89%)	$C_{12}H_{18}Cl_8$	414.9 (16%)	416.9 (3.1%)
$C_{11}H_{17}Cl_7$	360.9 (X+2)	362.9 (X+4, 80%)	$C_{13}H_{22}Cl_6$	361.0 (3.3%)	363.0 (0.2%)
$C_{11}H_{16}Cl_8$	394.9 (X+2)	396.9 (X+4, 96%)	$C_{13}H_{21}Cl_7$	395.0 (8.2%)	397.0 (1.0%)
$C_{11}H_{15}Cl_9$	430.9 (X+4)	428.9 (X+2, 89%)	$C_{13}H_{20}Cl_8$	428.9 (16%)	430.9 (3.1%)
$C_{12}H_{19}Cl_7$	374.9 (X+2)	376.9 (X+4, 80%)	$C_{14}H_{24}Cl_6$	375.0 (3.3%)	377.0 (0.2%)
$C_{12}H_{18}Cl_8$	408.9 (X+2)	410.9 (X+4, 96%)	$C_{14}H_{23}Cl_7$	409.0 (8.2%)	411.0 (1.0%)
$C_{12}H_{17}Cl_9$	444.9 (X+4)	442.9 (X+2, 89%)	$C_{14}H_{22}Cl_8$	442.9 (16%)	444.9 (3.1%)
$C_{13}H_{21}Cl_7$	389.0 (X+2)	391.0 (X+4, 80%)	$C_{15}H_{26}Cl_6$	389.0 (3.3%)	391.0 (0.2%)
$C_{13}H_{20}Cl_8$	422.9 (X+2)	424.9 (X+4, 96%)	$C_{15}H_{25}Cl_7$	423.0 (8.2%)	425.0 (1.0%)
$C_{13}H_{19}Cl_9$	458.9 (X+4)	456.9 (X+2, 89%)	$C_{15}H_{24}Cl_8$	456.9 (16%)	458.9 (3.1%)

Fig. 2 ECNI-mass chromatograms of the $[M-Cl]^-$ ions of $C_{10}H_{14}Cl_8$ (m/z 380.9) and of $C_{15}H_{26}Cl_6$ (m/z 383.0) for a SCCP standard, a MCCP standard and a 1+1 mixture of both, respectively



pendent relative abundance. Tomy et al. [12] and later Zencak et al. [13] showed that the relative abundance of the adduct ion is much higher for lower chlorinated congeners (4–5 chlorine atoms) than for higher chlorinated ones. The $[M+Cl]^-$ ion was the base ion for the investigated single tetrachlorodecanes, but it decreased to about 60% for the pentachlorodecane and 10% for the hexachlorodecane [13].

As can be seen from Table 4, the $[M+Cl]^-$ ions from SCCP congeners with 4–6 chlorine atoms can also cause mass overlap. $[M-Cl]^-$ anions from MCCP congeners with five carbon atoms more and the same number of chlorine atoms may also disturb SCCPs.

In CP mixtures with a low chlorine content (<50%) and therefore more congeners with four chlorine atoms, the resulting superposition of $[M-Cl]^-$ ions of SCCPs with $[M+Cl]^-$ ions of SCCPs with two chlorine atoms less could lead to an overestimation of congeners with five and six chlorine atoms. The latter can also mimic the presence of MCCP congeners with five carbon atoms more and the same

number of chlorine atoms. Such congeners are normally just detectable in MCCP mixtures with a chlorine content of <43%. Fortunately, the $[M+Cl]^-$ anions formed from MCCPs with low chlorine content (<50%) do not disturb the quantification of SCCPs. Zencak et al. [13] described a method to eliminate interferences between $[M+Cl]^-$ and $[M-Cl]^-$ ions by applying a mixture of CH_4/CH_2Cl_2 as reagent gas. This enhanced the formation of $[M+Cl]^-$ ions and suppressed the formation of $[M-Cl]^-$ ions for all congeners.

Linearity and detection limits

Linearity was investigated for two major congener groups ($C_{11}H_{18}Cl_6, C_{12}H_{20}Cl_6$) in the SCCP standard (55.5% chlorine content) and for two groups ($C_{14}H_{23}Cl_7, C_{15}H_{25}Cl_7$) in the MCCP standard (52% chlorine content). A good linearity, comparable to HRMS [7, 11], was achieved for LRMS between 1–100 ng of technical CPs for SCCPs and MCCPs ($R^2 > 0.993$, seven measuring points). The limit of

Table 4 Mass-to-charge ratios of $[M+Cl]^-$ ions of the most abundant isotopes of lower chlorinated short chain congeners, and the corresponding overlaps with the second most abundant isotope signals from $[M-Cl]^-$ ions of short chain congeners with the same number of carbons and two chlorines more. Interference with the $[M-Cl]^-$ ions of the most abundant isotope signals of MCCP congeners is also shown

^a Second most abundant isotope

Short chain CPs		Short chain CPs		Medium chain CPs	
CP congener	$[M+Cl]^-$ (M+Cl+2)	CP congener	$[M-Cl]^-$ (M-Cl+4)	CP congener	$[M-Cl]^-$ (M-Cl+2)
C ₁₀ H ₁₈ Cl ₄	315.0	C ₁₀ H ₁₆ Cl ₆	314.9 (64%)	C ₁₅ H ₂₈ Cl ₄	315.1 (96%) ^a
C ₁₀ H ₁₇ Cl ₅	348.9	C ₁₀ H ₁₅ Cl ₇	348.9 (80%)	C ₁₅ H ₂₇ Cl ₅	349.1
C ₁₀ H ₁₆ Cl ₆	382.9	C ₁₀ H ₁₄ Cl ₈	382.9 (96%)	C ₁₅ H ₂₆ Cl ₆	383.0
C ₁₁ H ₂₀ Cl ₄	329.0	C ₁₁ H ₁₈ Cl ₆	329.0 (64%)	C ₁₆ H ₃₀ Cl ₄	329.1 (96%) ^a
C ₁₁ H ₁₉ Cl ₅	362.9	C ₁₁ H ₁₇ Cl ₇	362.9 (80%)	C ₁₆ H ₂₉ Cl ₅	363.1
C ₁₁ H ₁₈ Cl ₆	396.9	C ₁₁ H ₁₆ Cl ₈	396.9 (96%)	C ₁₆ H ₂₈ Cl ₆	397.0
C ₁₂ H ₂₂ Cl ₄	343.0	C ₁₂ H ₂₀ Cl ₆	343.0 (64%)	C ₁₇ H ₃₂ Cl ₄	343.1 (96%) ^a
C ₁₂ H ₂₁ Cl ₅	377.0	C ₁₂ H ₁₉ Cl ₇	376.9 (80%)	C ₁₇ H ₃₁ Cl ₅	377.1
C ₁₂ H ₂₀ Cl ₆	410.9	C ₁₂ H ₁₈ Cl ₈	410.9 (96%)	C ₁₇ H ₃₀ Cl ₆	411.1

detection (LOD) for the two major components C₁₁H₁₈Cl₆ and C₁₂H₂₀Cl₆ of the SCCP mixture was 1 ng/μl of technical CPs at a signal-to-noise ratio of 3:1, and the limit of quantification (LOQ) was 2 ng/μl at a signal-to-noise ratio of 10:1. The LODs for the two major components C₁₄H₂₃Cl₇ and C₁₅H₂₅Cl₇ in the MCCP mixture were 0.5 and 1 ng/μl of technical MCCPs and the LOQs were 2.5 and 5 ng/μl, respectively. HRMS provides a better sensitivity. Analytical detection limits for major components of SCCPs and MCCPs were between ~60 pg and ~200 pg at a signal-to-noise ratio of 4:1 [7, 11]. However, the sensitivity of LRMS is well-suited for the analysis of CPs in the environment [10].

Conclusions

There is no doubt that using LRMS instead of HRMS will increase the risk of systematic errors due to mass interferences between different CP congeners, as discussed earlier. Nevertheless, the quantification of major congener groups is not affected by any interference (C₁₀ with 5–7 chlorine atoms, C₁₁, C₁₂ and C₁₃ with 5–8 chlorine atoms, C₁₄ with 5–9 chlorine atoms and C₁₅ with 7–9 chlorine atoms). However, the determination of C₁₀H₁₄Cl₈ and C₁₅H₂₆Cl₆ congeners can be disturbed if both are present in a sample. An evaluation of isotope ratios, retention time ranges and HRGC signal shapes allows us to detect such problems and to avoid a corresponding overestimation of their concentrations. However, this does not work for the quantification of C₁₆ and C₁₇ congeners, and will lead to values that are too high, if high levels of C₁₁ and C₁₂ congeners are present. Furthermore, the presence of SCCPs with nine and ten chlorine atoms can be mimicked by MCCPs, and vice versa for MCCPs with four and five chlorine

atoms by SCCPs. The sensitivity of LRMS is lower than for HRMS, but still appropriate for the determination of CPs in environmental samples. Also, despite the discussed interferences, the differentiation and simultaneous quantification of major SCCPs and MCCPs is still possible by LRMS.

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