

Supporting Information

Deconvolution of Mass Spectral Interferences of Chlorinated Alkanes and their Thermal Degradation Products: Chlorinated Alkenes

Lena Schinkel^{1,2,*}, Sandro Lehner^{1,3}, Norbert V. Heeb^{1,*}, Peter Lienemann³, Kristopher McNeill², Christian Bogdal⁴

¹Laboratory for Advanced Analytical Technologies, Swiss Federal Institute for Materials Science and Technology, Empa, Überlandstrasse 129, 8600 Dübendorf, Switzerland

²Institute of Biogeochemistry and Pollutant Dynamic, Swiss Federal Institute of Technology, ETH Zurich, Universitätsstrasse 16, 8092 Zurich, Switzerland

³Institute of Chemistry and Biotechnology, Zurich University of Applied Sciences, ZHAW, Grüentalstrasse 14, 8820 Wädenswil, Switzerland

⁴Institute for Chemical and Bioengineering, Swiss Federal Institute of Technology, ETH Zurich, Vladimir-Prelog-Weg 1, 8093 Zürich, Switzerland

* Corresponding authors: lena.schinkel@empa.ch, norbert.heeb@empa.ch, +41 58 765 4257.

Table of contents

1. Target ions	3
2. Full scan mass spectra of thermally exposed polychlorinated tridecanes over time	5
3. Deconvolution results	7
4. Quality of fit	10
5. Control: Thermolysis of 1,2,5,6,9,10-hexachlorodecane	11
6. First order rate constants and half-lives	13
7. Changes in chlorination degree	14

1. Target ions

Table S1. Chloride-adduct ions ($[M+Cl]^-$) of pentachlorinated tridecanes (CPs) and tridecenes (CP-enes) used for the deconvolution procedure.

$C_{13}H_{23}Cl_5$ (CPs)		$C_{13}H_{21}Cl_5$ (CP-enes)	
m/z	abund. in %	m/z	abund. in %
		386.9774	16.4
		387.9808	2.35
388.9931	16.4	388.9745	31.64
389.9965	2.35	389.9779	4.51
390.9902	31.63	390.9717	25.48
391.9936	4.52	391.9750	3.61
392.9873	25.48	392.9688	10.98
393.9906	3.62	393.9721	1.55
394.9845	10.98	394.9660	2.68
395.9877	1.55	395.9692	0.37
396.9817	2.68	396.9634	0.35

Table S2. Chloride-adduct ions ($[M+Cl]^-$) of hexachlorinated tridecanes (CPs) and tridecenes (CP-enes) used for the deconvolution procedure.

$C_{13}H_{22}Cl_6$ (CPs)		$C_{13}H_{20}Cl_6$ (CP-enes)	
m/z	abund. in %	m/z	abund. in %
		420.9385	12.43
		421.9419	1.78
422.9541	12.42	422.9356	27.95
423.9575	1.78	423.9389	3.98
424.9512	27.94	424.9327	26.98
425.9546	3.99	425.9360	3.83
426.9483	26.97	426.9298	14.5
427.9517	3.83	427.9331	2.05
428.9454	14.5	428.9270	4.69
429.9487	2.05	429.9302	0.66
430.9426	4.69	430.9242	0.92

Table S3. Chloride-adduct ions ($[M+Cl]^-$) of heptachlorinated tridecanes (CPs) and tridecenes (CP-enes) used for the deconvolution procedure.

$C_{13}H_{21}Cl_7$ (CPs)		$C_{13}H_{19}Cl_7$ (CP-enes)	
m/z	abund. in %	m/z	abund. in %
		454.8995	9.42
		455.9029	1.34
456.9151	9.41	456.8966	24.19
457.9186	1.35	457.9000	3.44
458.9122	24.18	458.8937	27.22
459.9156	3.45	459.8970	3.86
460.9093	27.21	460.8908	17.53
461.9127	3.87	461.8941	2.48
462.9064	17.52	462.8879	7.07
463.9097	2.48	463.8912	0.99
464.9036	7.07	464.8851	1.83
465.9068	0.99	465.8882	0.26
466.9007	1.83	466.8823	0.3

2. Full scan mass spectra of thermally exposed polychlorinated tridecanes over time

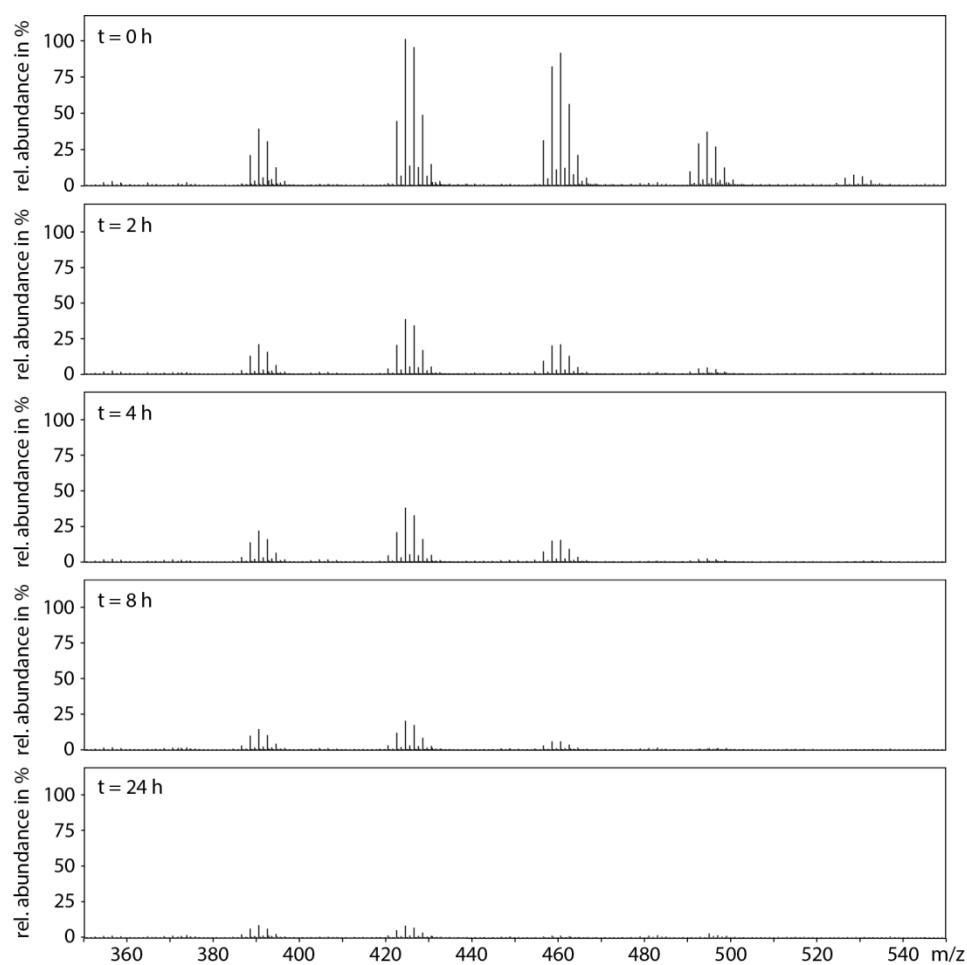


Figure S1. Measured spectra of thermally degraded polychlorinated tridecanes after 0, 2, 4, 8 and 24 h at 220°C. Abundances are related to the highest signal of the spectrum at 0 h. An overall loss in signal intensities can be observed. The displayed spectra are not IS-corrected. However signals of the internal standard are more or less constant among different samples.

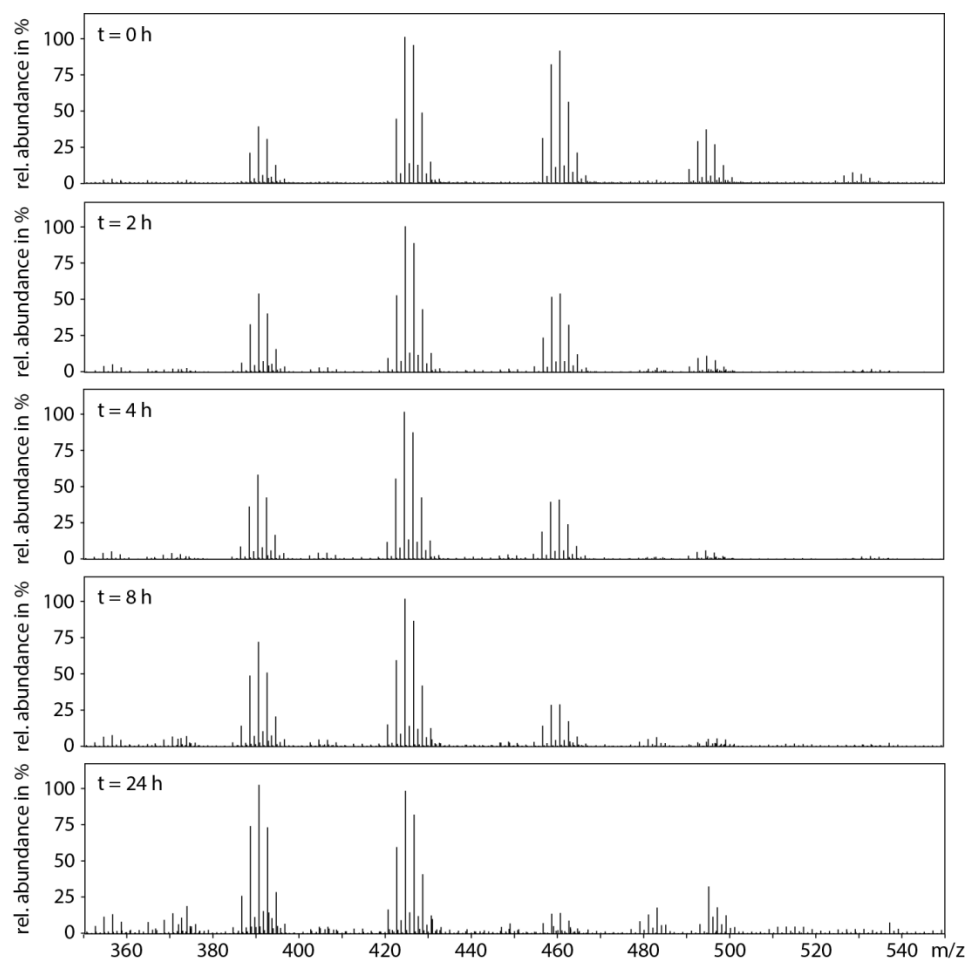


Figure S2. Measured spectra of thermally degraded polychlorinated tridecanes after 0, 2, 4, 8 and 24 h at 220°C. Abundances are related to the highest signal in each spectrum. A shift in abundance to lower chlorinated homologues is observed.

3. Deconvolution results

Table S4. Percentages of CPs (n_{CP}) and CP-enes (n_{ene}) after deconvolution of the different isotopic clusters.

Exposure time in h	Cl ₅ -cluster		Cl ₆ -cluster		Cl ₇ -cluster	
	n_{ene} in %	n_{CP} in %	n_{ene} in %	n_{CP} in %	n_{ene} in %	n_{CP} in %
0	<1	>99	3	97	<1	>99
2	22	78	22	78	20	80
4	27	73	26	74	23	77
8	36	64	33	67	28	72
24	44	56	37	63	n.q.	n.q.

n.q. – not quantified

Table S5. IS-corrected signal intensities of CPs (I_{CP100}) and their transformation products CP-enes (I_{ene100}) after deconvolution of the isotopic clusters

Exposure time in h	Cl ₅ -cluster		Cl ₆ -cluster		Cl ₇ -cluster	
	CP-ene in counts	CP in counts	CP-ene in counts	CP in counts	CP-ene in counts	CP in counts
0	n.d.	212100	18700	605100	n.d.	568400
2	43000	152400	85300	302400	45200	180900
4	44000	118800	79400	225900	30300	101400
8	31200	55500	43700	88700	11600	29800
24	19200	24400	16200	27600	n.q.	n.q.

n.d. – not detected

n.q. – not quantified

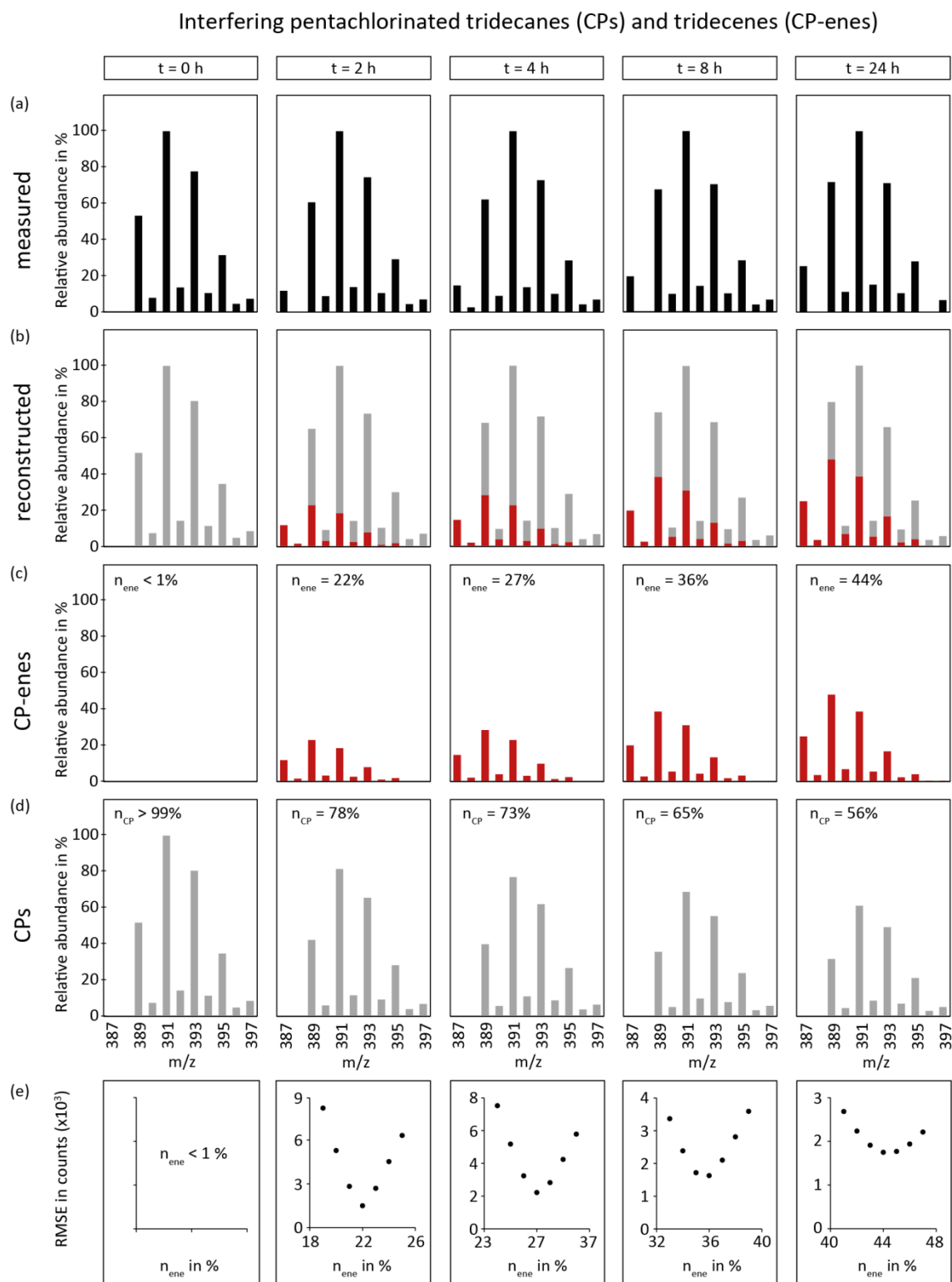


Figure S3. Deconvolution of interfering isotope patterns ($[M+Cl]^-$ adduct ions) of pentachlorinated tridecanes ($C_{13}H_{23}Cl_5$, grey) and pentachlorinated tridecenes ($C_{13}H_{21}Cl_5$, red), during 0, 2, 4, 8 and 24 h of thermal exposure at 220 °C. Changes in measured spectra (black) over time are shown (a) together with the deconvolved and reconstructed mass spectra (b), the CP-ene fraction (c, red) and the CP fraction (d, grey). Respective proportions, which increase from 1 to 44% for CP-enes and decrease accordingly from 99 to 56% for CPs are indicated. In addition RMSE is plotted vs. CP-ene fraction (e) to find minima of the respective least-RMSE function.

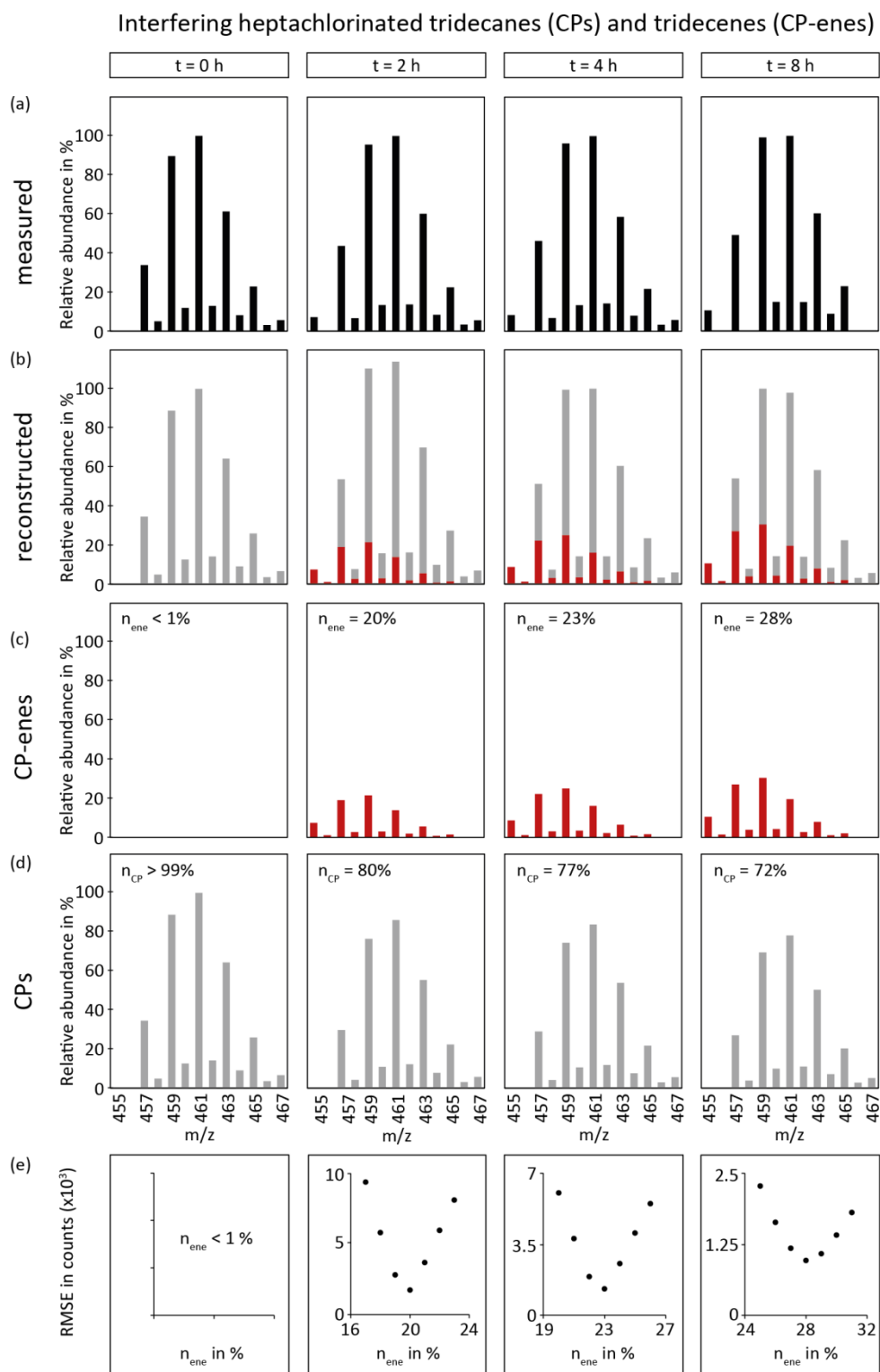


Figure S4. Deconvolution of interfering isotope patterns ($[M+Cl]^-$ adduct ions) of heptachlorinated tridecanes ($C_{13}H_{21}Cl_7$, grey) and heptachlorinated tridecenes ($C_{13}H_{19}Cl_7$, red), during 0, 2, 4 and 8 h of thermal exposure at 220 °C. Changes in measured spectra (black) over time are shown (a) together with the deconvolved and reconstructed mass spectra (b), the CP-ene fraction (c, red) and the CP fraction (d, grey). Respective proportions, which increase from 1 to 28% for CP-enes and decrease accordingly from 99 to 72% for CPs are indicated. In addition RMSE is plotted vs. CP-ene fraction (e) to find minima of the respective least-RMSE function.

4. Quality of fit

The quality of fit is represented by the coefficient of determination R^2 , which is calculated using the following equation:

$$R^2 = 1 - \frac{\sum_i (y_i - f_i)^2}{\sum_i (y_i - \bar{y})^2}$$

f_i : measured signal intensity of a specific ion i

y_i : modelled intensity of the ions i in the reconstructed cluster after deconvolution

\bar{y} : mean of the modelled intensities of all ions (y_i) in the cluster.

Table S6. Quality of fit (R^2) for the deconvolved and reconstructed clusters for interfering CPs and CP-enes with 5, 6 and 7 chlorines respectively.

t in h	R^2		
	Cl ₅ -cluster	Cl ₆ -cluster	Cl ₇ -cluster
0	1.00	1.00	1.00
2	1.00	1.00	1.00
4	1.00	1.00	1.00
8	0.99	1.00	0.99
24	0.99	1.00	-

5. Control: Thermolysis of 1,2,5,6,9,10-hexachlorodecanes

In order to prove with an independent method, that chlorinated alkenes indeed are thermal transformation products of CPs, a 1,2,5,6,9,10-hexachlorodecanes mixture with defined constitution (by Dr Ehrensdoerfer) was exposed to 220°C for 0, 2 and 8 h. Using this material, pentachlorodecanes, those CPs that would interfere with the expected transformation product, are absent. Hence, a formation of pentachlorodecenes (CP-enes) can be observed without mass interferences. At 0 h, the mass spectrum is dominated by the chloride-adduct cluster ($[M+Cl]^-$ adduct ions) of hexachlorodecane and only traces (2%) of pentachlorodecene (CP-ene) are present (Figure S5). Over time, the relative abundance of CPs (n_{CP}) decreases from 98% to 61%, whereas the abundance of CP-enes (n_{ene}) increases from 2% to 39%, for 0 h and 8 h thermal exposure, respectively.

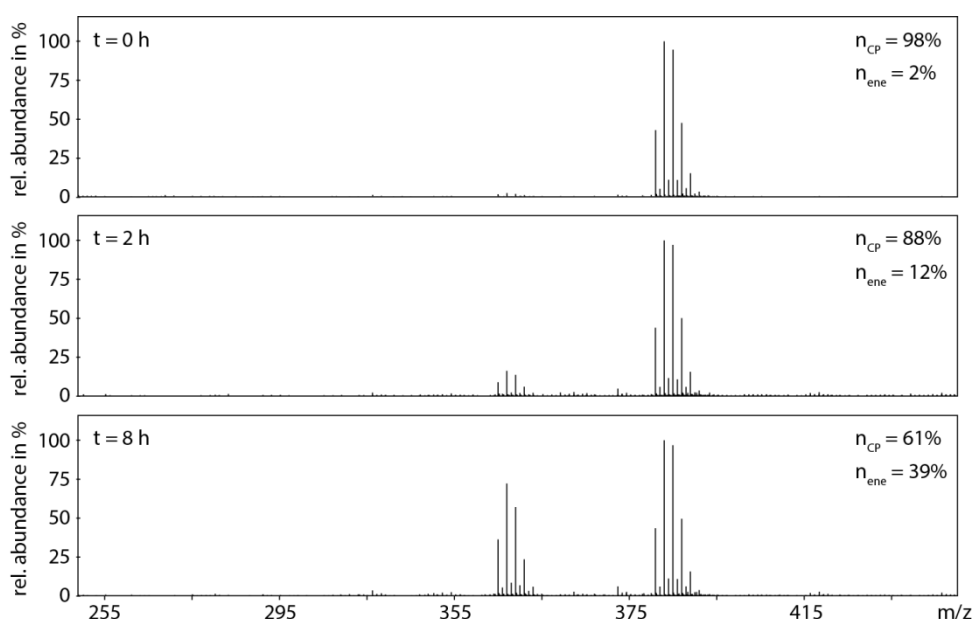


Figure S5. Measured spectra of thermally degraded 1,2,5,6,9,10-hexachlorodecanes after 0, 2, and 8 h at 220°C. Abundances are related to the highest signal in each spectrum. At the beginning, the mass spectrum is dominated by the $[M+Cl]^-$ cluster of hexachlorodecanes (CPs). The formation of pentachlorodecenes (CP-enes) is observed over time, whose relative abundance (n_{ene}) increases from 2% to 12% to 39% at 0, 2 and 8 h.

For hexachlorodecanes (CPs), proportions of ions within the measured clusters match the theoretical cluster and are therefore not interfered (Figure S6). In the non-exposed material, the intensity of the ion cluster of pentachlorodecenes (CP-enes) is very low, resulting in slight deviations from the theoretical cluster. After 8 h exposure, intensity of CP-enes is higher and the ion cluster is identical to the theoretical one. The cluster is therefore not interfered, as well (Figure S6).

For $t=0$ h, three independent samples were prepared and processed, to investigate statistical deviations. The IS-corrected intensity of CP-enes (I_{ene100}) at 8 h accounted 39800 counts which is four

times higher than in the starting material (10000 ± 3400 counts), confirming a statistically significant formation of CP-enes (Figure S6).

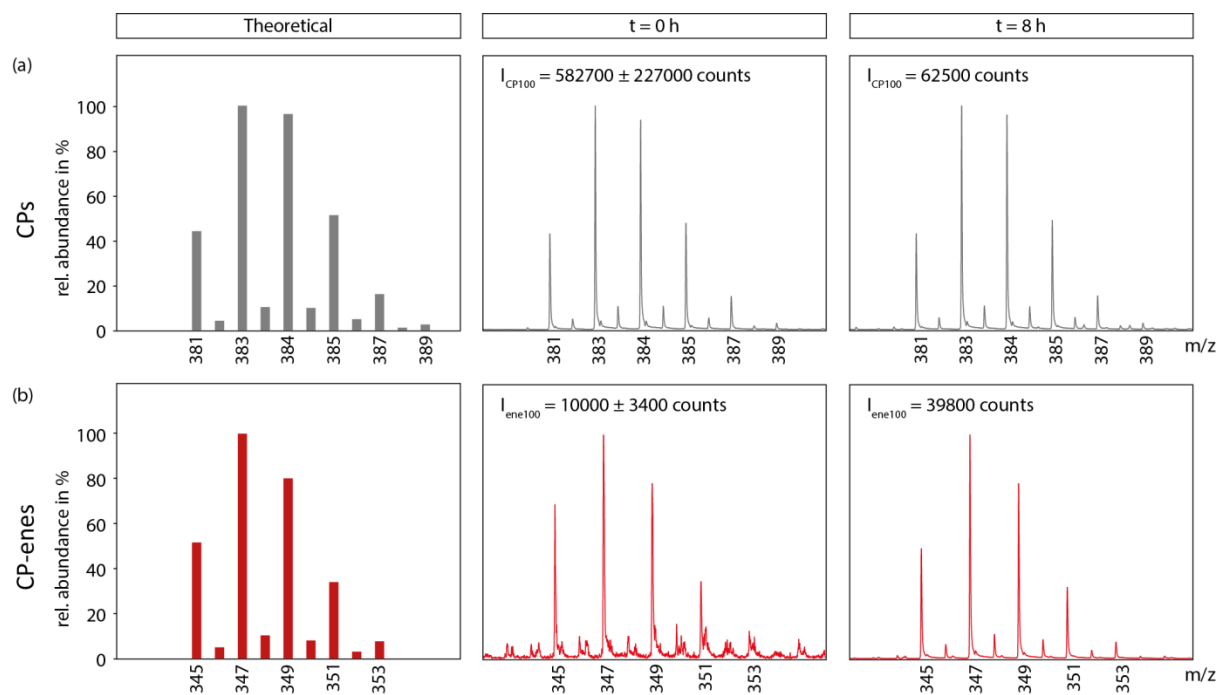


Figure S6. Theoretical and measured isotopic clusters ($[M+Cl]^-$) for (a) hexachlorodecanes (CPs) and (b) pentachlorodecenenes (CP-enes). For CPs, the measured clusters match the theoretical one and are therefore not interfered. The intensity of the CP-ene cluster at 0 h is low, resulting in slight deviations from the theoretical cluster. However, CP-ene cluster after 8 h exposure is identical to the theoretical one. IS-corrected intensity of CP-ene (I_{ene100}) after exposure is four times higher than at start, confirming the transformation of hexachlorodecanes to pentachlorodecenenes by HCl-elimination.

6. First order rate constants and half-lives

Table S7. First order rate constants for thermolysis of different polychlorinated tridecane homologues determined by linear regression of $\ln(I_t/I_0)$ versus time (Figure 5c, main text of this publication) and corresponding half-lives for thermal degradation at 220°C.

Polychlorinated tridecane	Rate constant k in h^{-1}	Half-lives $t_{1/2}$ in h
Cl ₅	0.16	4.3
Cl ₆	0.25	2.8
Cl ₇	0.39	1.8

7. Changes in chlorination degree

Changes in chlorination degree over time are calculated based on the deconvolved Cl₅-, Cl₆- and Cl₇-clusters. Figure S7 shows a steady shift to lower chlorinated compounds during exposure to heat. Other homologues, such as the Cl₈- and Cl₉-clusters also contribute to some degree, but were not considered here, since deconvolution was not carried out for those clusters, due to low signal intensities. As can be seen in Figure S1, their contributions are expected to be small. The signal intensity of Cl₇-cluster was too low at 24 h, not allowing for deconvolution of the cluster and respective chlorination degree was not calculated. However, at 24 h exposure, the chlorination degree also decreased (Figure S2), but could not be calculated accurately, due to lacking information about the Cl₇-cluster.

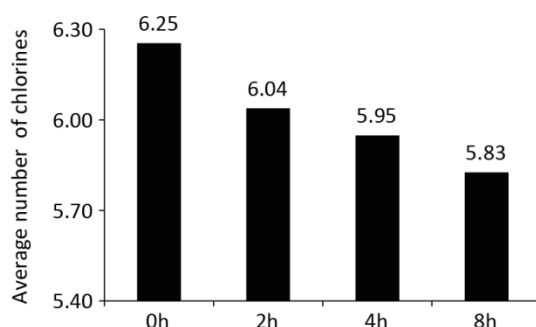


Figure S7. Decrease of the chlorination degree and thus the average number of chlorine atoms of the studied Cl₅-, Cl₆- and Cl₇-clusters. To calculate overall degree of chlorination, the remaining Cl₄-, Cl₈-, Cl₉-clusters need to be considered, as well. Measurement at 24 h was not included, because the abundance of the Cl₇-cluster was too low to deconvolve CPs and CP-enes.

Calculating the average number of chlorine

During the deconvolution procedure, the signal intensities of CP-enes (I_{ene100}) and CPs (I_{CP100}) are calculated which represent the combined signal intensity of all ions within a CP or CP-ene cluster (Table S5). Signal-intensities for CPs and CP-enes are summed up for each Cl₅-, Cl₆- and Cl₇-cluster, to get the sum count for each reconstructed cluster within a sample. Corresponding proportions of the Cl₅-, Cl₆- and Cl₇-clusters were calculated, converted into the average number of chlorine atoms per sample and reported in Figure S7.