

Supplementary Information

Method validation and comparison of quantification strategies for analysis of chlorinated paraffins in indoor dust by liquid chromatography and high-resolution mass spectrometry

Thomas J. McGrath^a, Adrian Covaci^a, Giulia Poma^a

^aToxicological Centre, University of Antwerp, Universiteitsplein 1, 2610, Wilrijk, Belgium

Table S1. SCCP and MCCP parameters for monitored in $[M+Cl]^-$ ions.

C-chain length	Cl number	Quantifier m/z	Qualifier m/z	Ratio*	C-chain length	Cl number	Quantifier m/z	Qualifier m/z	Ratio*
10	4	314.9827	316.9798	0.64	14	4	371.0453	373.0424	0.64
10	5	348.9437	350.9408	0.80	14	5	405.0063	407.0034	0.80
10	6	382.9048	384.9018	0.97	14	6	438.9674	440.9644	0.96
10	7	418.8629	416.8658	0.89	14	7	474.9255	472.9284	0.89
10	8	452.8239	450.8268	0.78	14	8	508.8865	506.8894	0.78
10	9	486.7849	488.7820	0.86	14	9	542.8475	544.8446	0.86
10	10	520.7459	522.7430	0.96	14	10	576.8085	578.8056	0.96
10	11	556.7040	554.7070	0.93	14	11	612.7666	610.7696	0.94
10	12	590.6650	588.6680	0.85	14	12	646.7276	644.7306	0.85
11	4	328.9984	330.9954	0.64	15	4	385.0610	387.0580	0.64
11	5	362.9594	364.9564	0.80	15	5	419.0220	421.0190	0.80
11	6	396.9204	398.9175	0.97	15	6	452.9830	454.9801	0.96
11	7	432.8785	430.8815	0.89	15	7	488.9411	486.9441	0.89
11	8	466.8395	464.8425	0.78	15	8	522.9021	520.9051	0.78
11	9	500.8006	502.7976	0.86	15	9	556.8632	558.8602	0.86
11	10	534.7616	536.7586	0.96	15	10	590.8242	592.8212	0.96
11	11	570.7197	568.7226	0.93	15	11	626.7823	624.7852	0.93
11	12	604.6807	602.6836	0.85	15	12	660.7433	658.7462	0.85
12	4	343.0140	345.0111	0.64	16	4	399.0766	401.0737	0.64
12	5	376.9750	378.9721	0.80	16	5	433.0376	435.0347	0.80
12	6	410.9361	412.9331	0.97	16	6	466.9987	468.9957	0.96
12	7	446.8942	444.8971	0.89	16	7	502.9568	500.9597	0.89
12	8	480.8552	478.8581	0.78	16	8	536.9178	534.9207	0.78
12	9	514.8162	516.8133	0.86	16	9	570.8788	572.8759	0.86
12	10	548.7772	550.7743	0.96	16	10	604.8398	606.8369	0.96
12	11	584.7353	582.7383	0.93	16	11	640.7979	638.8009	0.94
12	12	618.6963	616.6993	0.85	16	12	674.7589	672.7619	0.85
13	4	357.0297	359.0267	0.64	17	4	413.0923	415.0893	0.64
13	5	390.9907	392.9877	0.80	17	5	447.0533	449.0503	0.80
13	6	424.9517	426.9488	0.96	17	6	481.0143	483.0114	0.96
13	7	460.9098	458.9128	0.89	17	7	516.9724	514.9754	0.89
13	8	494.8708	492.8738	0.78	17	8	550.9334	548.9364	0.78
13	9	528.8319	530.8289	0.86	17	9	584.8945	586.8915	0.86
13	10	562.7929	564.7899	0.96	17	10	618.8555	620.8525	0.96
13	11	598.7510	596.7539	0.94	17	11	654.8136	652.8165	0.93
13	12	632.7120	630.7149	0.85	17	12	688.7746	686.7775	0.85

Table S2. LCCP parameters for monitored in [M+Cl]⁻ ions.

C-chain length	Cl number	Quantifier m/z	Qualifier m/z	Ratio*	C-chain length	Cl number	Quantifier m/z	Qualifier m/z	Ratio*
18	4	427.1079	429.1050	0.64	22	4	483.1705	485.1676	0.64
18	5	461.0689	463.0660	0.80	22	5	517.1315	519.1286	0.80
18	6	495.0300	497.0270	0.96	22	6	551.0926	553.0(He <i>et al.</i> , 2019)[1]896	0.96
18	7	530.9881	528.9910	0.89	22	7	587.0507	585.0536	0.89
18	8	564.9491	562.9520	0.78	22	8	621.0117	619.0146	0.78
18	9	598.9101	600.9072	0.86	22	9	654.9727	656.9698	0.86
18	10	632.8711	634.8682	0.96	22	10	688.9337	690.9308	0.97
18	11	668.8292	666.8322	0.93	22	11	724.8918	722.8948	0.93
18	12	702.7903	700.7932	0.85	22	12	758.8529	756.8558	0.85
19	4	441.1236	443.1206	0.64	23	4	497.1862	499.1832	0.64
19	5	475.0846	477.0816	0.80	23	5	531.1472	533.1442	0.80
19	6	509.0456	511.0427	0.96	23	6	565.1082	567.1053	0.96
19	7	545.0037	543.0067	0.89	23	7	601.0663	599.0693	0.89
19	8	578.9647	576.9677	0.78	23	8	635.0273	633.0303	0.78
19	9	612.9258	614.9228	0.86	23	9	668.9884	670.9854	0.86
19	10	646.8868	648.8838	0.96	23	10	702.9494	704.9465	0.96
19	11	682.8449	680.8478	0.94	23	11	738.9075	736.9104	0.93
19	12	716.8059	714.8089	0.85	23	12	772.8685	770.8715	0.85
20	4	455.1392	457.1363	0.64	24	4	511.2018	513.1989	0.64
20	5	489.1002	491.0973	0.80	24	5	545.1629	547.1599	0.80
20	6	523.0613	525.0583	0.96	24	6	579.1239	581.1209	0.96
20	7	559.0194	557.0223	0.89	24	7	615.0820	613.0849	0.89
20	8	592.9804	590.9833	0.78	24	8	649.0430	647.0459	0.78
20	9	626.9414	628.9385	0.86	24	9	683.0040	685.0011	0.86
20	10	660.9025	662.8995	0.96	24	10	716.9651	718.9621	0.96
20	11	696.8605	694.8635	0.94	24	11	752.9231	750.9261	0.94
20	12	730.8216	728.8245	0.85	24	12	786.8842	784.8871	0.85
21	4	469.1549	471.1519	0.64	25	4	525.2175	527.2145	0.64
21	5	503.1159	505.1129	0.80	25	5	559.1785	561.1756	0.80
21	6	537.0769	539.0740	0.96	25	6	593.1395	595.1366	0.96
21	7	573.0350	571.0380	0.89	25	7	629.0976	627.1006	0.89
21	8	606.9960	604.9990	0.78	25	8	663.0586	661.0616	0.78
21	9	640.9571	642.9541	0.86	25	9	697.0197	699.0167	0.85
21	10	674.9181	676.9152	0.97	25	10	730.9807	732.9778	0.96
21	11	710.8762	708.8791	0.93	25	11	766.9388	764.9418	0.94
21	12	744.8372	742.8402	0.85	25	12	800.8999	798.9028	0.85

Section S1. Chlorine-content quantification

Samples were quantified by chlorine-content calibration using a modified version of the Reth *et al.* (2005) method (equations 1-5 below). Technical standards of SCCPs (51.5, 55.5 and 63 %Cl), MCCPs (42, 52 and 57 %Cl) and LCCPs (36 and 49%Cl) were used to make calibration standards at 5 degrees of Cl% for each group, each with a total concentration of 4.0 µg/mL. All calibrants contained the internal standard, ¹³C-β-HBCD, at 200 ng/mL. Samples were then quantified using exponential calibration curves constructed from the total relative response factors and calculated chlorine content. Response of the ¹³C-β-HBCD internal standard was used to derive relative responses for individual CP homologue groups

For each calibration point (*CP Cal*), *Total Response Factor (TRF)* and *Chlorine Content* were calculated as follows:

(1)

$$\text{Relative Total Area (CP Cal)} = \sum_i \frac{\text{Area (Congener Group } i)}{\text{Area (S } i)}$$

where *i* refers to analysed congener groups per SCCP, MCCP or LCCP calibration standard and S refers to the response of ¹³C-β-HBCD from the corresponding injection.

(2)

$$\text{Total Response Factor (CP Cal)} = \frac{\text{Relative Total CP Area (CP Cal)}}{\text{Concentration (CP Cal)}}$$

(3)

$$\begin{aligned} \text{Chlorine Content (CP Cal)} \\ = \sum_i \frac{\text{Relative Area (Congener Group } i) \times \text{Chlorine Content (Congener Group } i)}{\text{Relative Total Area (CP Cal)}} \end{aligned}$$

Where *Relative Area* refers to the area of the congener group divided by area of the ¹³C-β-HBCD standard and *Chlorine Content* refers to the mass percentage of Cl in the congener group.

Chlorine Content vs Total Response Factor were plotted for the ΣSCCP, ΣMCCP and ΣLCCP calibration standards and each were fit with exponential regression curves. Exponential equations derived from calibration plots were then used to calculate concentrations in sample extracts as follows:

(4)

$$\text{Total Response Factor (Sample)} = ae^{b \times \text{Chlorine Content (Sample)}}$$

where a and b are coefficients from the exponential curves fit to the calibration standards for Σ SCCPs, Σ MCCPs and Σ LCCPs and *Chlorine Content (Sample)* was calculated with equation (3) using LC-QTOF responses from the sample.

(5)

$$CP \text{ Concentration (Sample)} = \frac{\text{Relative Total Area (Sample)}}{\text{Total Response Factor (Sample)}}$$

Where *Relative Total Area* and *Total Response Factor* are calculated using equations (1) and (2), respectively, with LC-QTOF responses for the sample.

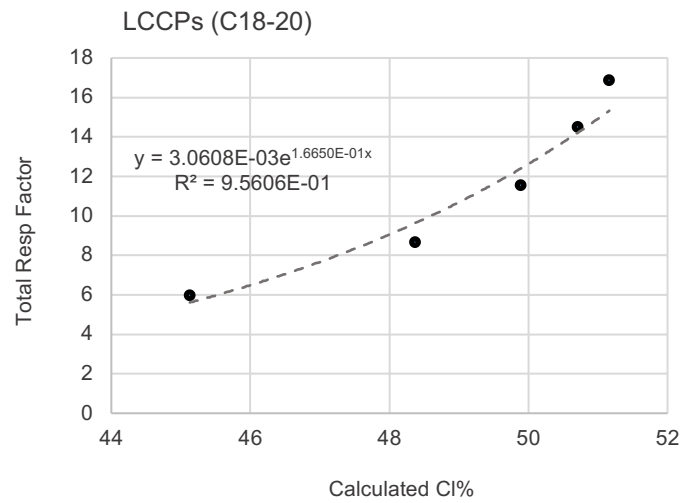
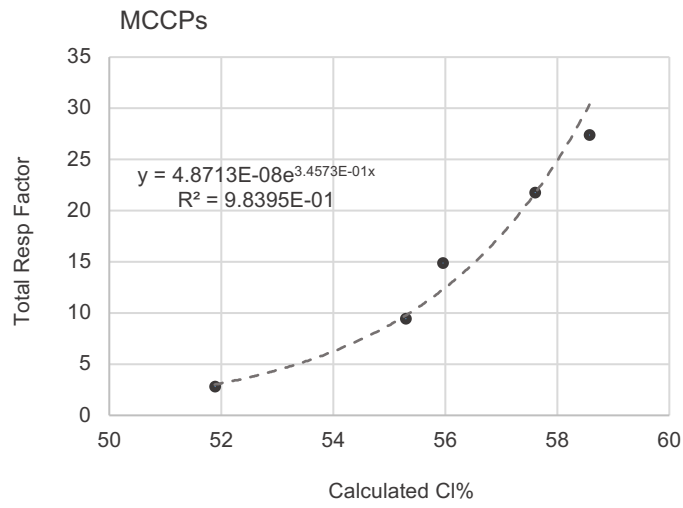
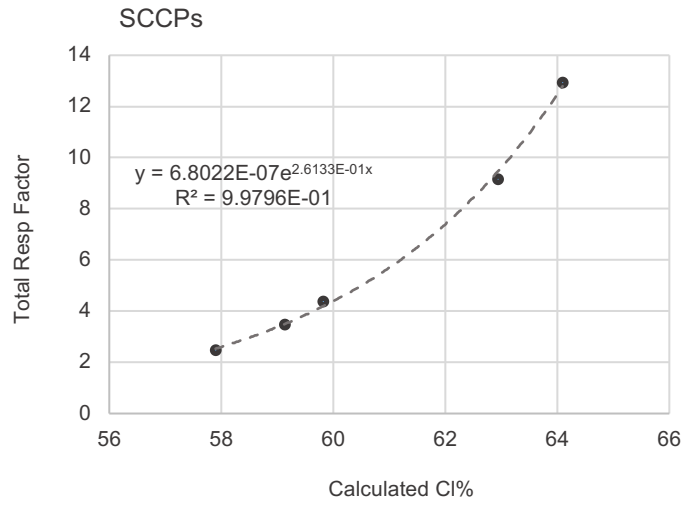


Figure S1. Calibration curves for chlorine-content quantification of SCCPs, MCCPs and LCCPs. Determination of total response factor and calculated Cl% are described in Section S1.

Section S2. Human exposure assessment

Estimates of daily exposure to CPs were calculated using the following equation;

$$\Sigma \text{Exposure via dust ingestion (ng/kg bw/day)} = \frac{[(C_O F_O) + (C_H F_H)] I_R}{\text{Body Weight}}$$

where C_O and C_H are the analyte concentrations in offices and homes, respectively, F_O and F_H are the proportions of time spent in offices and homes, respectively and I_R is the daily dust ingestion rate. Exposure estimates have been computed using median concentrations for each environment and differentiate adults (>18 years) and toddlers (6 to 24 months). The proportion of time spent in offices and homes were designated as 22 and 69%, respectively, for adults and 0 and 91% for toddlers (Harrad *et al.*, 2006; Basis & Samara, 2012; De Wit *et al.*, 2012). Mean and high dust intake scenarios were calculated using mean dust ingestion rates of 20 mg/day for adults and 50 mg/day for toddlers and high ingestion rates of 50 mg/day and 200 mg/day for toddlers (Ali *et al.*, 2013; Harrad *et al.*, 2016). Body weights of 70 and 12 Kg were assigned for adults and toddlers, respectively (EFSA, 2012). As in previous studies of exposure to organohalogen contaminants (De Wit *et al.*, 2012; Ali *et al.*, 2013; Hassan & Shoeib, 2015), 100% uptake of all compounds has been assumed in exposure estimates due to a lack of evidence regarding bioavailability of CPs. Although it is acknowledged that this may lead to an overestimation of exposure, this approach has been chosen to provide a conservative assessment of risk.

Table S3. Composition of spike mixtures A-I.

Spike mixture ID	Technical standards	Spike ratio
A	SCCP 51.5%Cl :	50 : 50 : 0
B	SCCP 55.5%Cl :	0 : 100 : 0
C	SCCP 63%Cl	0 : 50 : 50
D	MCCP 42%Cl :	50 : 50 : 0
E	MCCP 52%Cl :	0 : 100 : 0
F	MCCP 57%Cl	0 : 50 : 50
G		75 : 25
H	LCCP 36%Cl :	50 : 50
I	LCCP 49%Cl	25 : 75

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