

SUPPORTING INFORMATION

DETERMINATION OF POLYCHLORINATED BIPHENYLS IN SOLID SAMPLES BY ISOTOPE DILUTION MASS SPECTROMETRY USING ³⁷Cl-LABELED ANALOGUES

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Number of pages. 13

Number of Figures: 12

Number of Tables: 3

EXPERIMENTAL PROCEDURES

Table S1. Experimental parameters employed for GC-MS/MS measurements.

CHROMATOGRAPHIC PARAMETERS	
Chromatograph	7890A Agilent Technologies
Column	DB-5MS (30 m x 0.25 mm i.d. x 0.250 μ m coating)
Carrier gas	He (2 mL/min)
Injection mode	Splitless (2 min of purge time)
Injector temperature	280°C
Temperature program	From 80°C (1 min) 220°C (0 min) at 20°C/min 232°C (0 min) at 5°C/min 300°C (3 min) at 30°C/min
DETECTOR PARAMETERS	
Detector	Agilent 7000
Ionization current	35 μ A
Ionization energy	70 eV
Source temperature	230°C
Interface temperature	280°C
Dwell time	100 ms

Synthesis of the ^{37}Cl -enriched PCBs

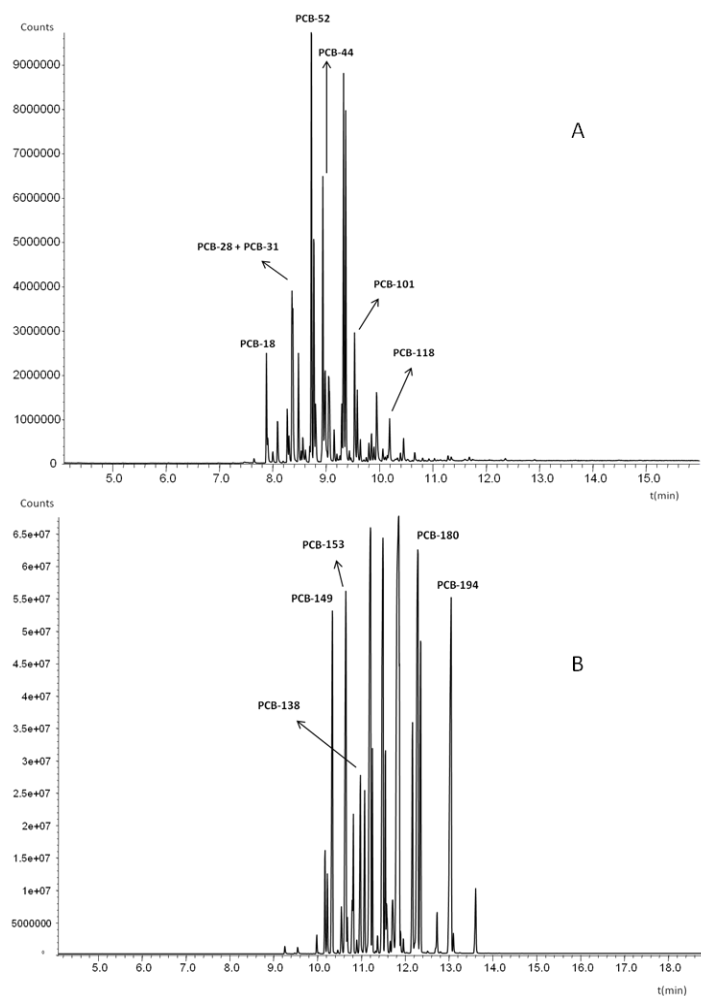


Figure S1. GC-MS chromatogram of A) the less chlorinated synthesis crude obtained when using 12.5 mg of biphenyl and B) the highly chlorinated synthesis crude obtained when using 5.5 mg of biphenyl.

Isolation and purification of the of the ^{37}Cl -enriched PCBs

The HPLC instrumental system was equipped with a Zorbax Eclipse XDB-C18 (9.4 mm, 250 mm, 5 μm) separation column. The column flow and the wavelength for UV detection were set at 2.5 mL/min and 254 nm, respectively. A volume of 100 μL of both synthesis crudes was injected in the system and the fractions corresponding to the twelve target congeners were collected using an analytical-scale fraction collector. Figure S2 shows the resulting HPLC-UV chromatograms of both synthesis crudes.

Similarly than Figure S1, Figure S2 also shows that a high number of PCBs congeners were synthesized in both crudes.

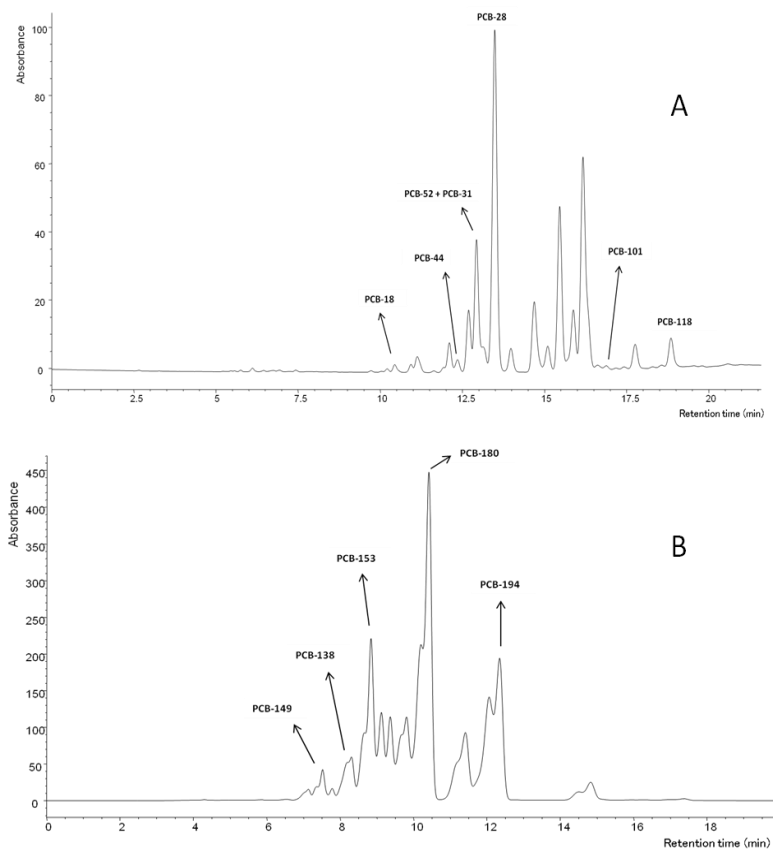


Figure S2. HPLC-UV Chromatograms of A) the less chlorinated synthesis crude obtained when using 12.5 mg of biphenyl using a mobile phase of 80% ACN and 20% H₂O and B) the highly chlorinated synthesis crude obtained when using 5.5 mg of biphenyl using 100% ACN as mobile phase.

After the identification of the target PCBs by the retention times injecting individual natural abundance standards, the collection time window for each fraction was defined for each of the target PCBs. Then these fractions were injected in a GC-MS system in Scan mode in order to identify all co-eluting PCBs in each fraction. For some congeners, a second HPLC separation using a different mobile phase composition and the subsequent GC-MS analysis was required. After a successful purification of the twelve target PCBs, we prepared a mixture containing the twelve congeners to be used in further experiments for the analysis of the samples.

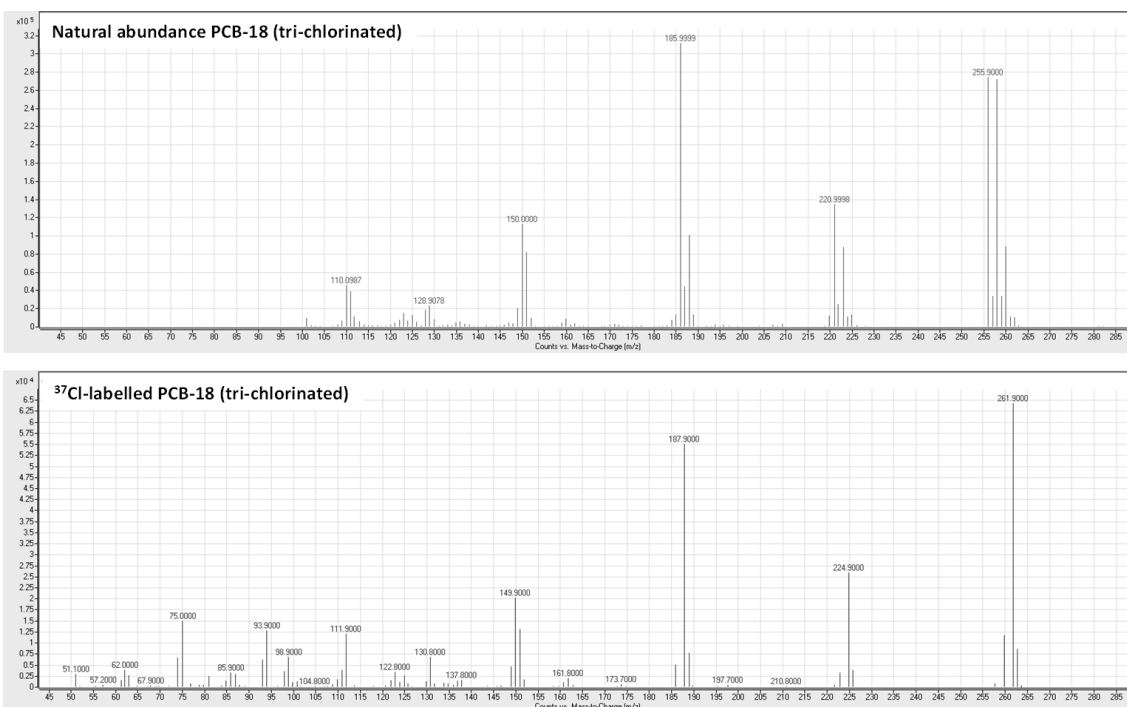


Figure S3. Comparison of the GC-MS mass spectra obtained in SCAN mode of the tri-chlorinated natural abundance and the ³⁷Cl-labeled PCB 18.

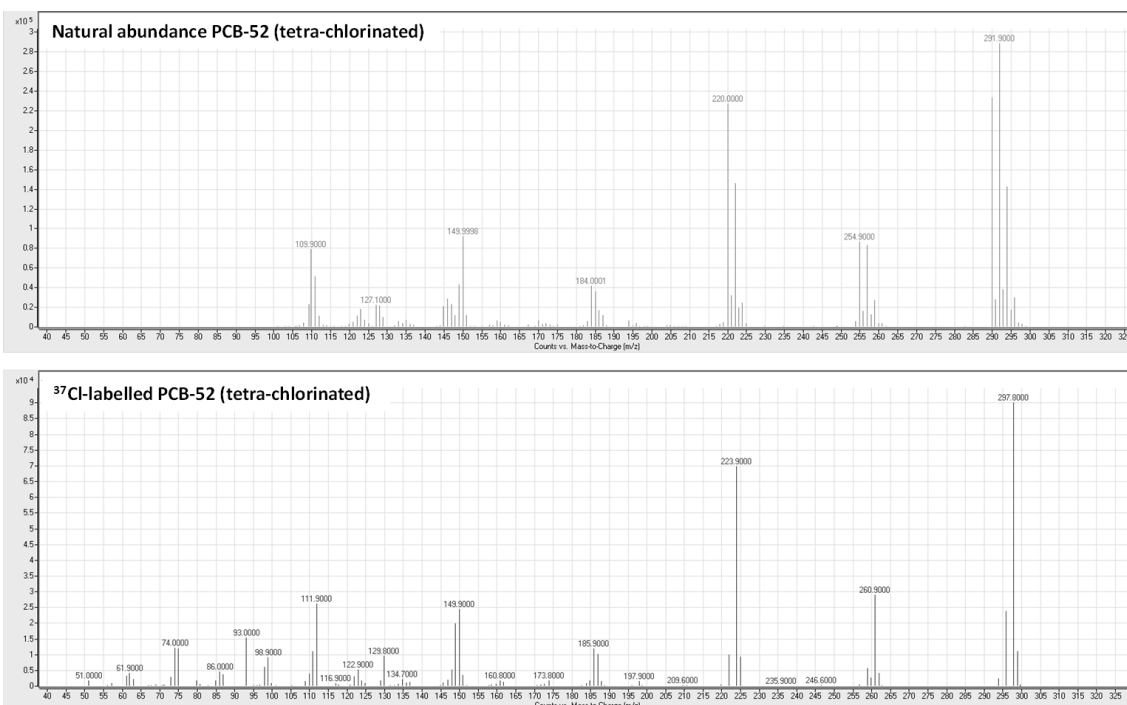


Figure S4. Comparison of the GC-MS mass spectra obtained in SCAN mode of the tetra-chlorinated natural abundance and the ³⁷Cl-labeled PCB 52.

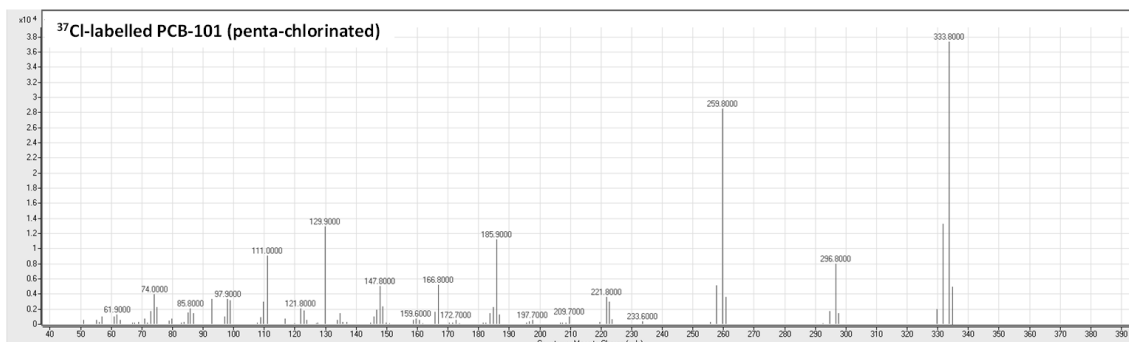
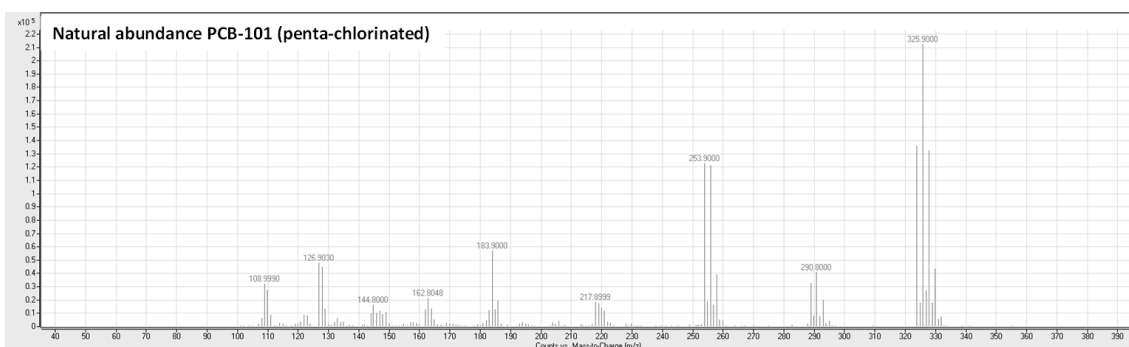


Figure S5. Comparison of the GC-MS mass spectra obtained in SCAN mode of the penta-chlorinated natural abundance and the ^{37}Cl -labelled PCB 101.

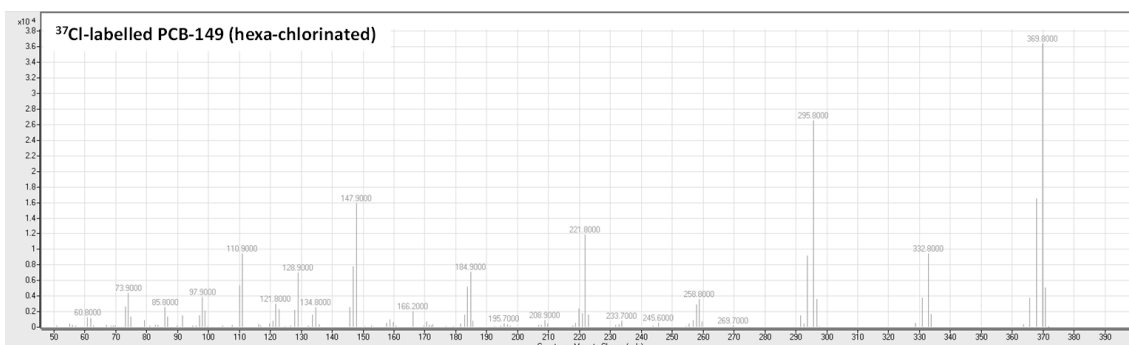
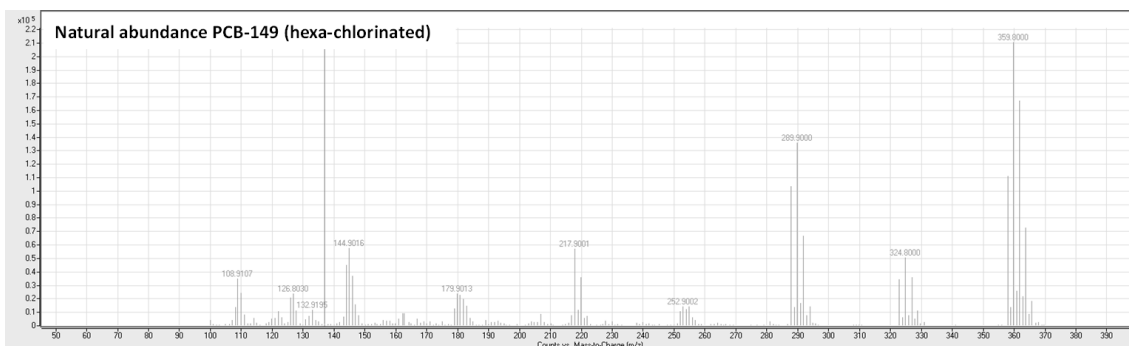


Figure S6. Comparison of the GC-MS mass spectra obtained in SCAN mode of the hexa-chlorinated natural abundance and the ^{37}Cl -labelled PCB 149.

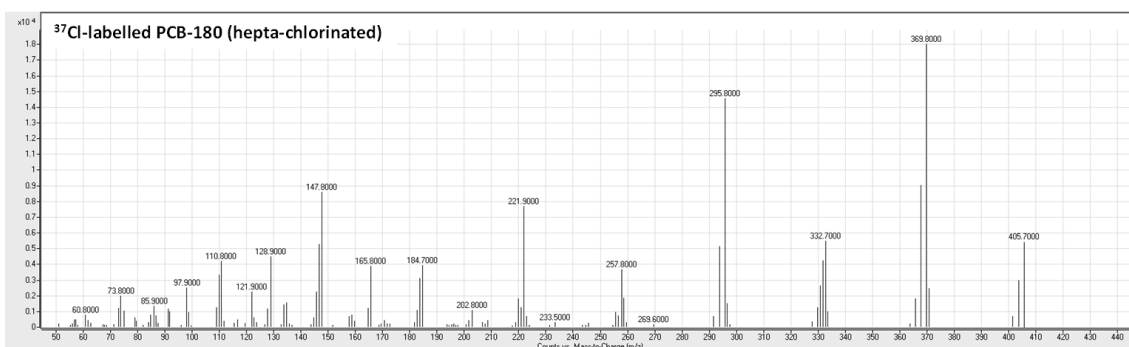
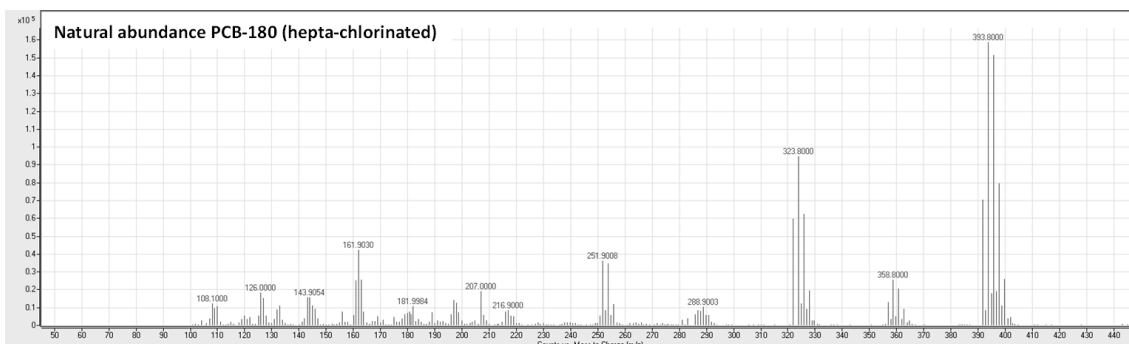


Figure S7. Comparison of the GC-MS mass spectra obtained in SCAN mode of the hepta-chlorinated natural abundance and the ^{37}Cl -labelled PCB 180.

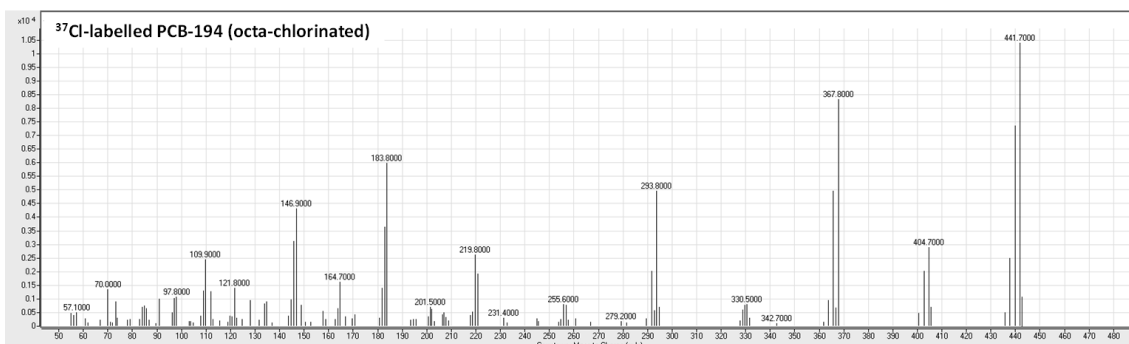
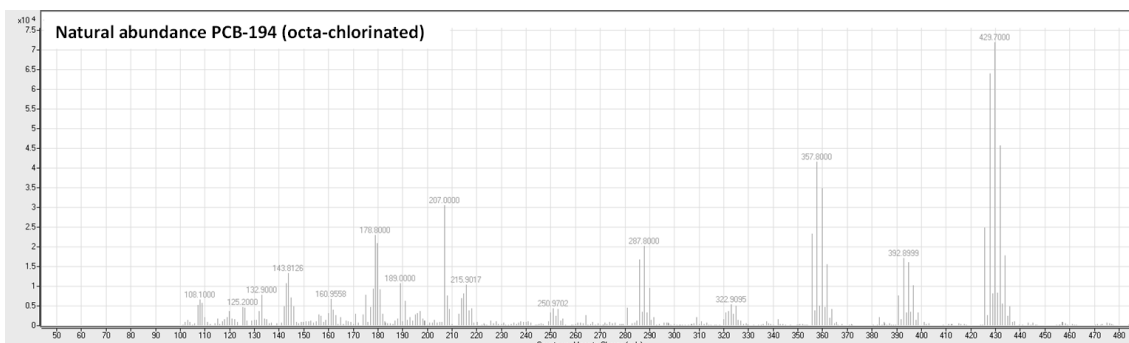


Figure S8. Comparison of the GC-MS mass spectra obtained in SCAN mode of the octa-chlorinated natural abundance and the ^{37}Cl -labelled PCB 194.

Table S2. Isotopic enrichment and concentration of the ^{37}Cl -labeled PCB congeners synthesised in this work. Uncertainty of the isotopic enrichments corresponds to the standard deviation of n=6 independent determinations. Uncertainty of the concentrations corresponds to the standard deviation of n=7 determinations carried out over a period of 6 months.

PCB congener	Number of Cl atoms	Isotopic enrichment ^{37}Cl(%)	Concentration (ng g⁻¹)
18	3	94.14 ± 0.06	1147 ± 25
28+31	3	94.05 ± 0.04	1927 ± 25
44	4	94.16 ± 0.03	947 ± 35
52	4	94.06 ± 0.03	1008 ± 26
101	5	94.06 ± 0.06	1028 ± 34
118	5	93.99 ± 0.03	1015 ± 32
138	6	92.51 ± 0.02	1421 ± 55
149	6	92.70 ± 0.03	1049 ± 47
153	6	92.70 ± 0.03	804 ± 54
180	7	91.93 ± 0.03	1079 ± 53
194	8	91.45 ± 0.03	1346 ± 22

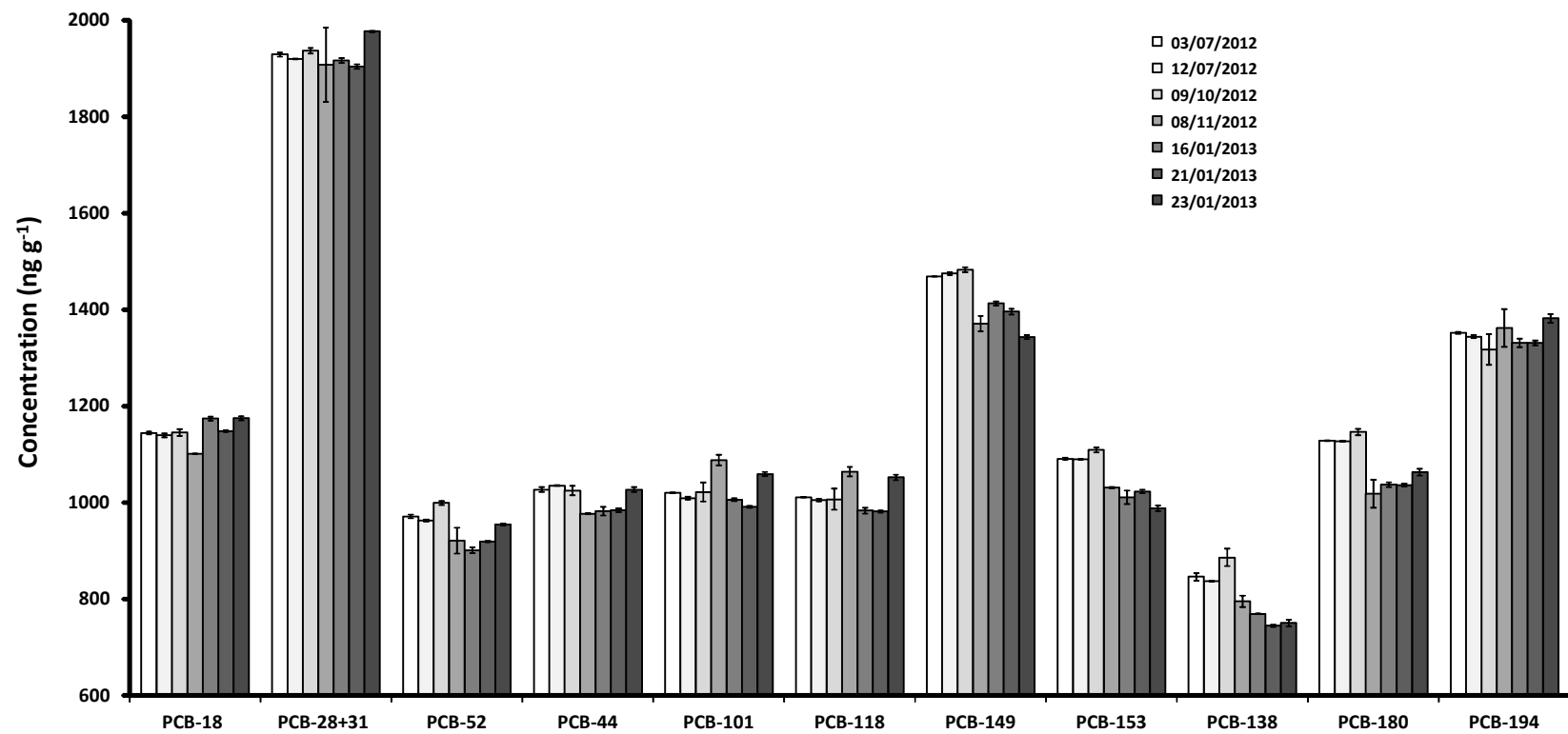


Figure S9. Concentration of the ^{37}Cl -enriched PCBs synthesised in this work over a period of six months. Error bars correspond to the uncertainty of three independent blends expressed as 1s standard deviation.

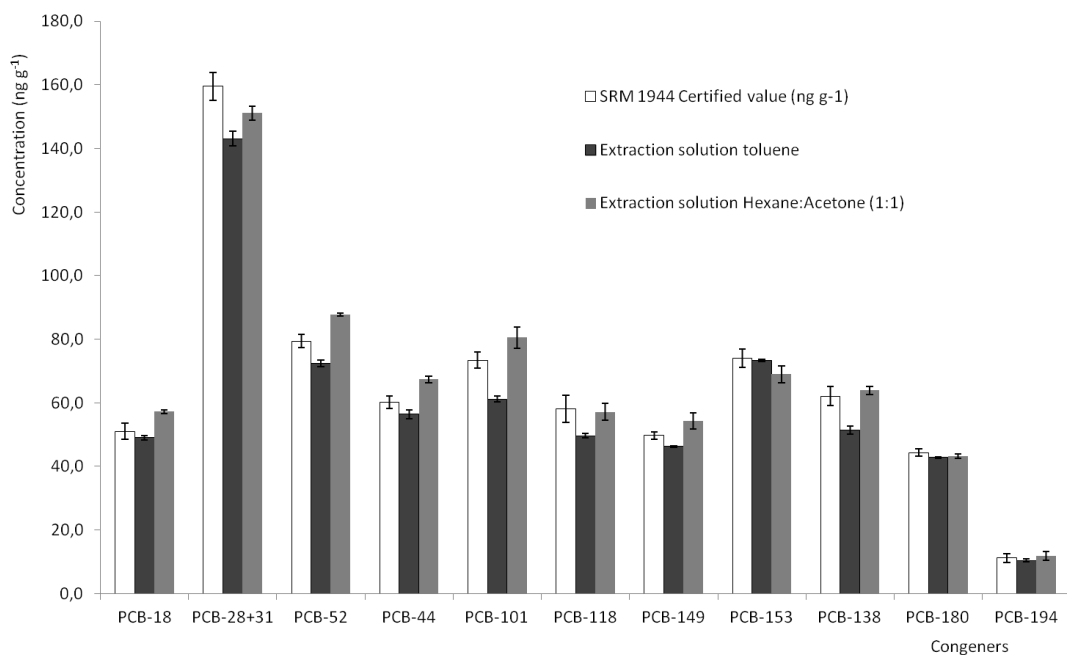


Figure S10. Comparison of the certified and experimental concentrations obtained in the analysis of the certified sediment SRM1944 when using toluene and a 1:1 mixture of hexane and acetone. Error bars of the experimental values correspond to the 1s standard deviation of three independent extractions.

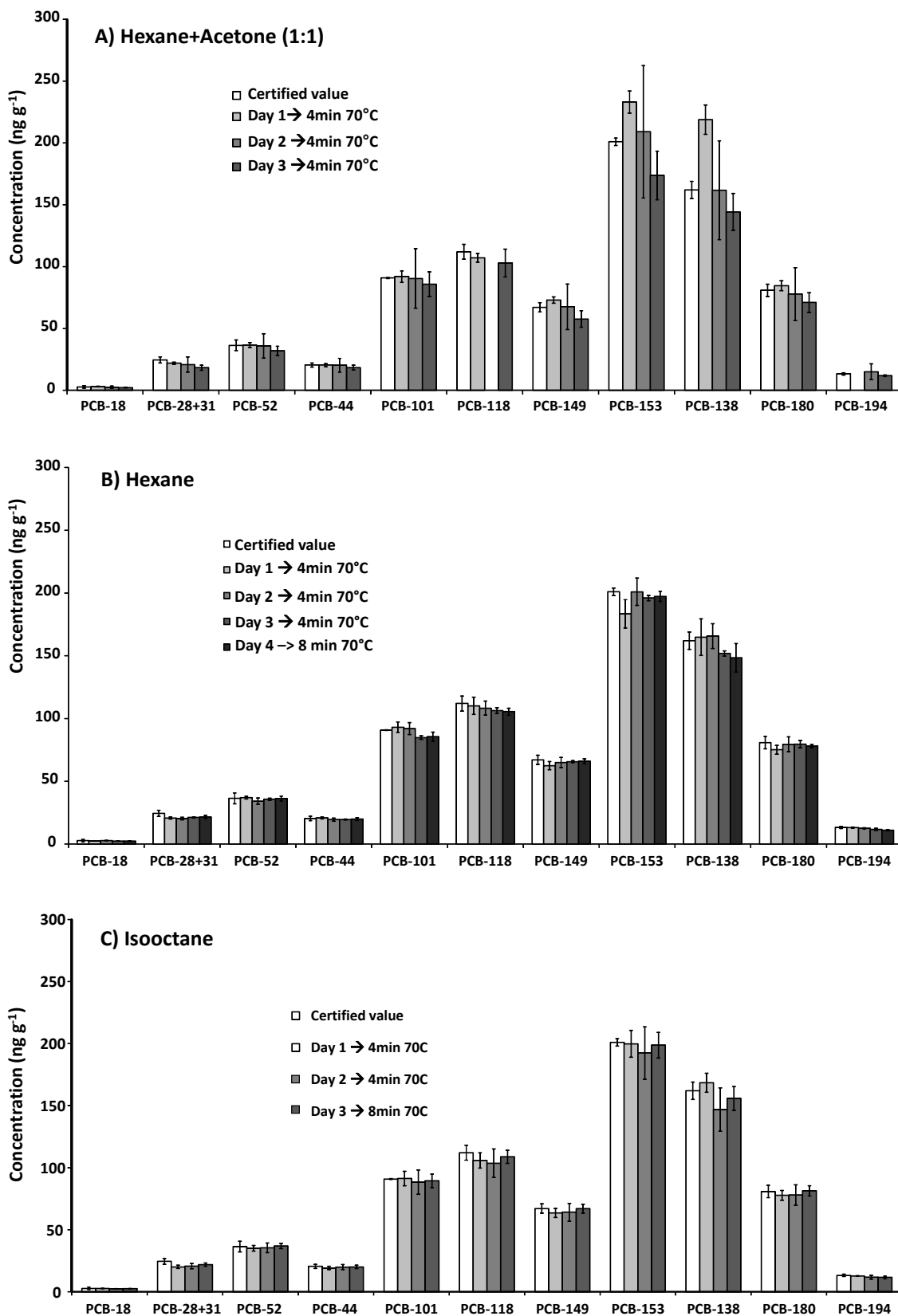


Figure S11. Comparison of the certified and experimental concentrations obtained in the analysis of the certified fish tissue SRM 1947 under different extraction conditions when using as extractant A) a 1:1 mixture of hexane and acetone, B) Hexane and C) Isooctane. Error bars of the experimental values correspond to the 1s standard deviation of three independent extractions

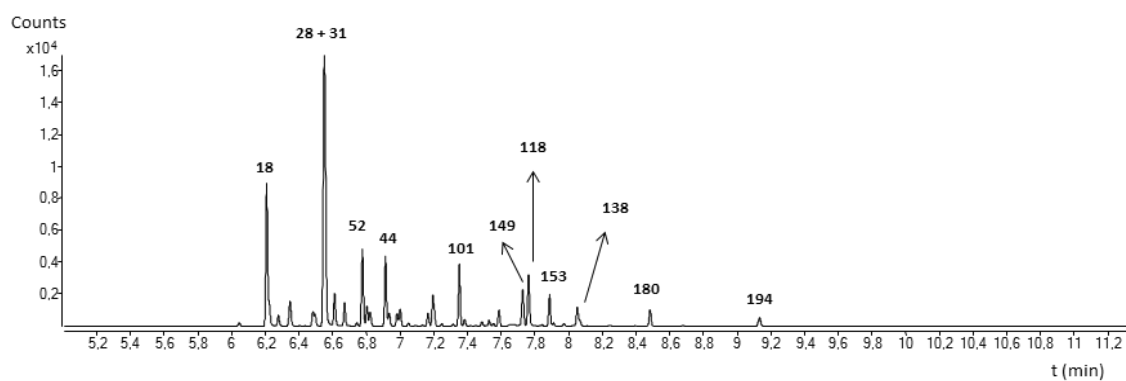


Figure S12. GC-MS/MS chromatogram of the reference material SRM1944 New York/New Jersey waterway sediment spiked with 70 ng the ³⁷Cl- enriched PCBs.

Table S3. Blank values (in ng g⁻¹) and resulting Limit of Detection obtained for all target PCB congeners except for PCB 180 and PCB-194.

Day	Replicates	PCB-18 (ng g ⁻¹)	PCB-28+31 (ng g ⁻¹)	PCB-52 (ng g ⁻¹)	PCB-44 (ng g ⁻¹)	PCB-101 (ng g ⁻¹)	PCB-118 (ng g ⁻¹)	PCB-149 (ng g ⁻¹)	PCB-153 (ng g ⁻¹)	PCB-138 (ng g ⁻¹)
Day 1	1	0.174±0.019	0.529 ± 0.031	0.801 ± 0.017	0.534 ± 0.040	0.894 ± 0.033	0.500 ± 0.071	0.363 ± 0.104	0.412 ± 0.184	0.298 ± 0.136
	2	0.114 ± 0.015	0.343 ± 0.016	0.487 ± 0.024	0.315 ± 0.033	0.362 ± 0.021	0.151 ± 0.049	0.150 ± 0.010	0.177 ± 0.015	0.215 ± 0.017
	3	0.113 ± 0.029	0.357 ± 0.017	0.503 ± 0.032	0.344 ± 0.033	0.369 ± 0.073	0.128 ± 0.050	0.155 ± 0.010	0.184 ± 0.012	0.227 ± 0.014
Day 2	1	0.117 ± 0.003	0.524 ± 0.065	0.687 ± 0.047	0.499 ± 0.044	0.784 ± 0.066	0.336 ± 0.049	0.293 ± 0.074	0.182 ± 0.038	0.134 ± 0.035
	2	0.110 ± 0.011	0.451 ± 0.018	0.613 ± 0.024	0.422 ± 0.011	0.660 ± 0.010	0.362 ± 0.015	0.301 ± 0.045	0.197 ± 0.017	0.152 ± 0.020
	3	0.114 ± 0.008	0.490 ± 0.011	0.778 ± 0.006	0.518 ± 0.012	0.870 ± 0.030	0.454 ± 0.027	0.382 ± 0.034	0.266 ± 0.021	0.216 ± 0.015
Average (ng g⁻¹)		0.124	0.449	0.645	0.438	0.657	0.322	0.274	0.236	0.207
Standard Deviation (S_B)		0.052	0.185	0.273	0.186	0.332	0.186	0.138	0.123	0.095
Limit of Detection (3S_B)		0.16	0.56	0.82	0.56	0.99	0.56	0.42	0.39	0.28