Reproducible trace analysis of PCBs in environmental matrices using triple quadrupole GC-MS/MS

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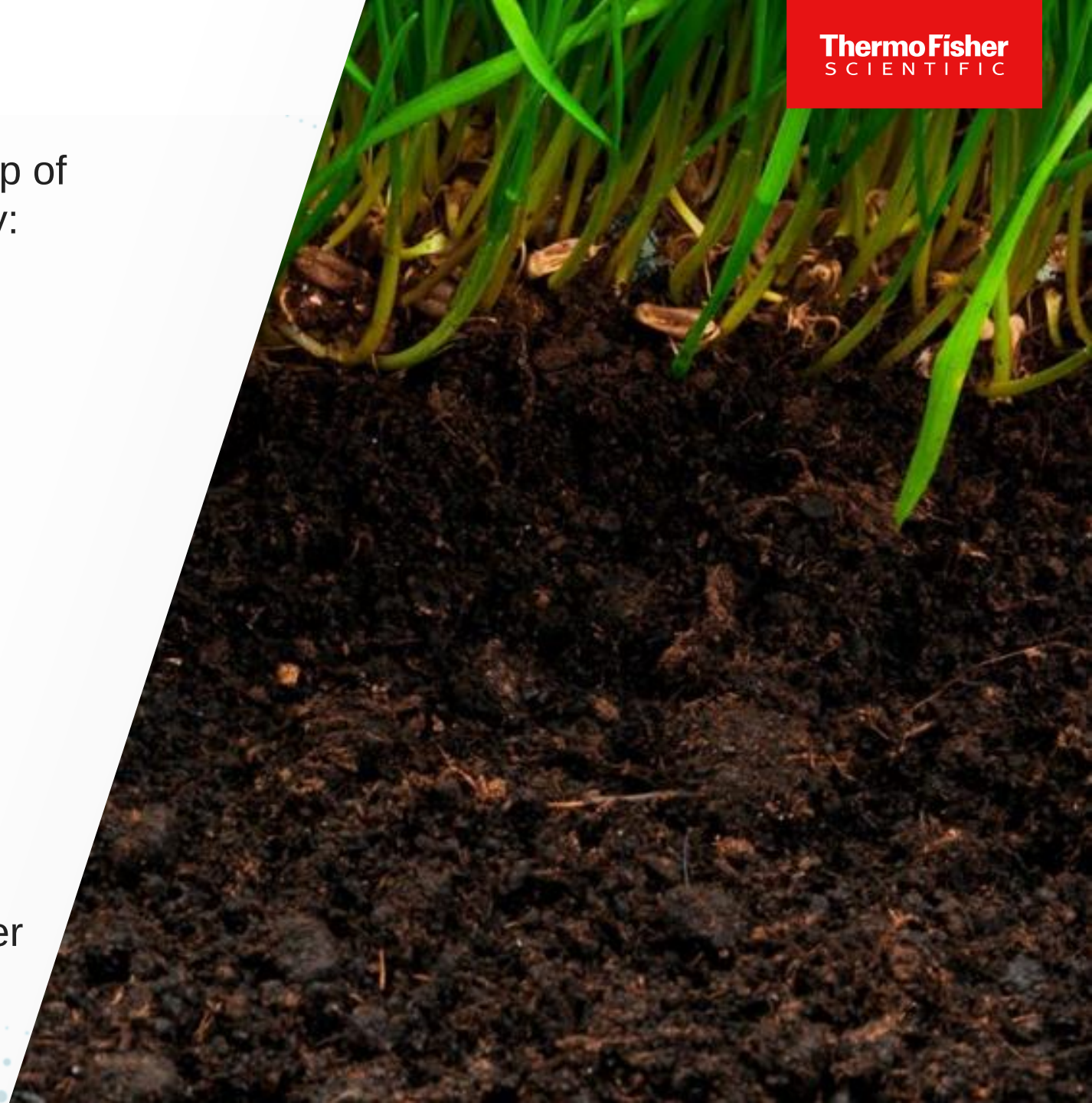
Content

Introduction

Polychlorinated biphenyls (PCBs) are a group of industrial organic chemicals characterized by:

- non-flammability
- chemical stability
- high boiling point
- electrical insulating properties
- persistence in environment

Many of these properties make PCBs historically useful in electrical insulators, hydraulic equipment, paints, rubbers, and other industrial applications



PCB congeners

Currently 209 known PCBs congeners that can be divided into two groups according to their structural and toxicological characteristics:

- non-dioxin like PCBs (non-DL-PCB):
  - majority of the PCB congeners
  - lower degree of toxicity

- dioxin-like PCBs (DL-PCBs):
  - the 12 most toxic congeners
  - classified as POPs
  - regulated under the Stockholm Convention for POPs since 2001

PCB Regulation

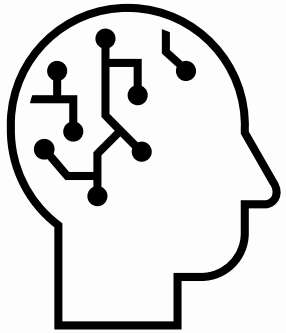
- Because of toxicity/mutagenicity and persistence in the environment, particularly in soils and waters, PCBs are highly regulated in many countries
- PCB clean-up and remediation can prove challenging due to their tenacity
- Although the goal for PCBs in water is zero in the US, the maximum contaminant level is set at 0.5 ppb.

GC-MS/MS for analysis of PCBs

- EPA developed Method 1668 using GC-HRMS
- Advances in GC-MS/MS allows for reliable application to PCB analysis.
  - Different extraction and clean-up processes
  - More sensitive/selective mass analyzers and column phases
  - Re-evaluation of performance metrics
- Important parameters to consider:
  - Working range, particularly on the low-end
  - Linearity, reproducibility, robustness
  - Applicability for routine analysis.

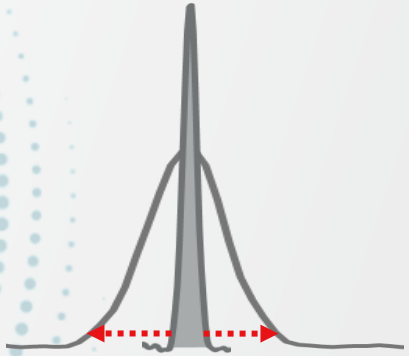
Traditional Challenges

Challenges



- Complicated sample preparation

- Sufficient chromatographic separation between PCBs needed to avoid isobaric interferences



- Long run times for sufficient separations. Low throughput and high costs.

Analytical Parameters

AI/AS 1610 autosampler parameters	
Injection type	Standard
Sample mode	Standard
Fill strokes	10
Sample depth	Bottom
Injection mode	Fast
Pre-injection delay time (s)	0
Post-injection delay time (s)	0
Pre-injection wash cycles	0
Post-injection wash cycles	4
Post-injection solvent wash volume (µL)	6.0
Sample wash cycles	1
Sample wash volume (µL)	1.0
Injection volume (µL)	1.0

SSL parameters	
Injection temperature (°C)	280
Liner	Thermo Scientifc™ LinerGOLD™ splitless/split liner single taper with wool (P/N 453A1925-UI)
Inlet module and mode	SSL, splitless
Split flow (mL/min)	75
Splitless time (min)	1.2
Septum purge flow (mL/min)	5, constant
Carrier gas, flow (mL/min)	He, 1.2

TRACE 1610 GC parameters	
Oven temperature program	
Temperature (°C)	90
Hold time (min)	1.00
Rate (°C/min)	25
Temperature 2 (°C)	270
Rate 2 (°C/min)	4
Temperature 3 (°C)	330
Hold time (min)	2
GC run time (min)	25.20
Column	
TRACE TR-PCB 8 MS	50 m, 0.25 mm, 0.25 µm (P/N 26AJ148P)

TSQ 9610 mass spectrometer parameters	
Transfer line temperature (°C)	280
Ion source type and temperature (°C)	NeverVent AEI, 300
Ionization type	EI
Emission current (µA)	50
Aquisition mode	timed-SRM
Q1 and Q3 resolution	Normal (0.7 amu)
Tuning parameters	AEI SmartTune
Collision gas and pressure (psi)	Argon at 70
Detector gain	X 7

Sample preparation for environmental matrices

Aqueous samples (1L) containing less than 1% solid

Separatory funnel extraction

Clean-up with acid and/or base silica gel and Alumina chromatography

Concentration of extract to 10-50 µL prior to GC injection

Solid, semi-solid, and multi-phase samples (10 g dry weight)

Soxhlet extraction

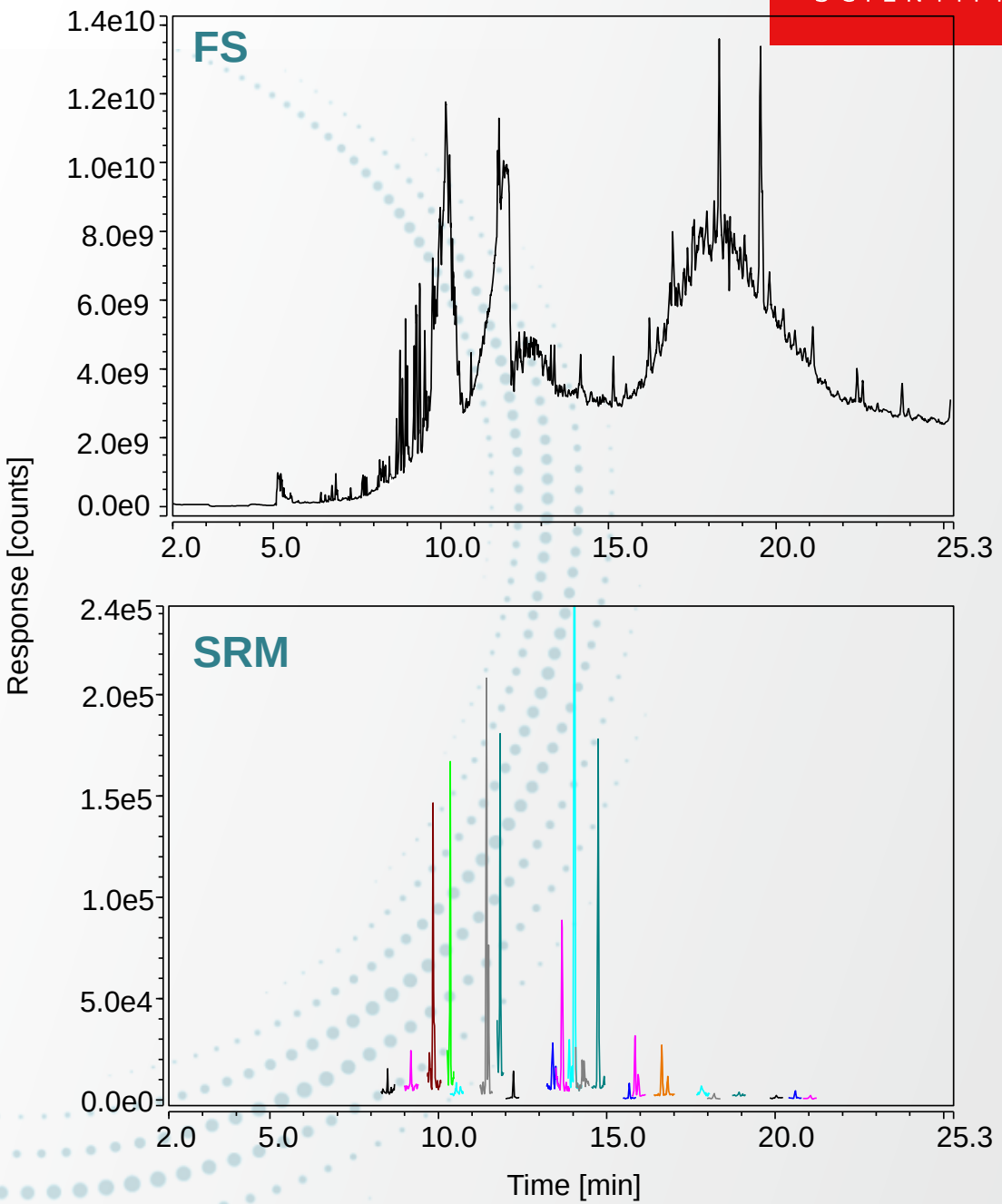
Clean-up with acid and/or base silica gel and Alumina chromatography

Concentration of extract to 10-50 µL prior to GC injection

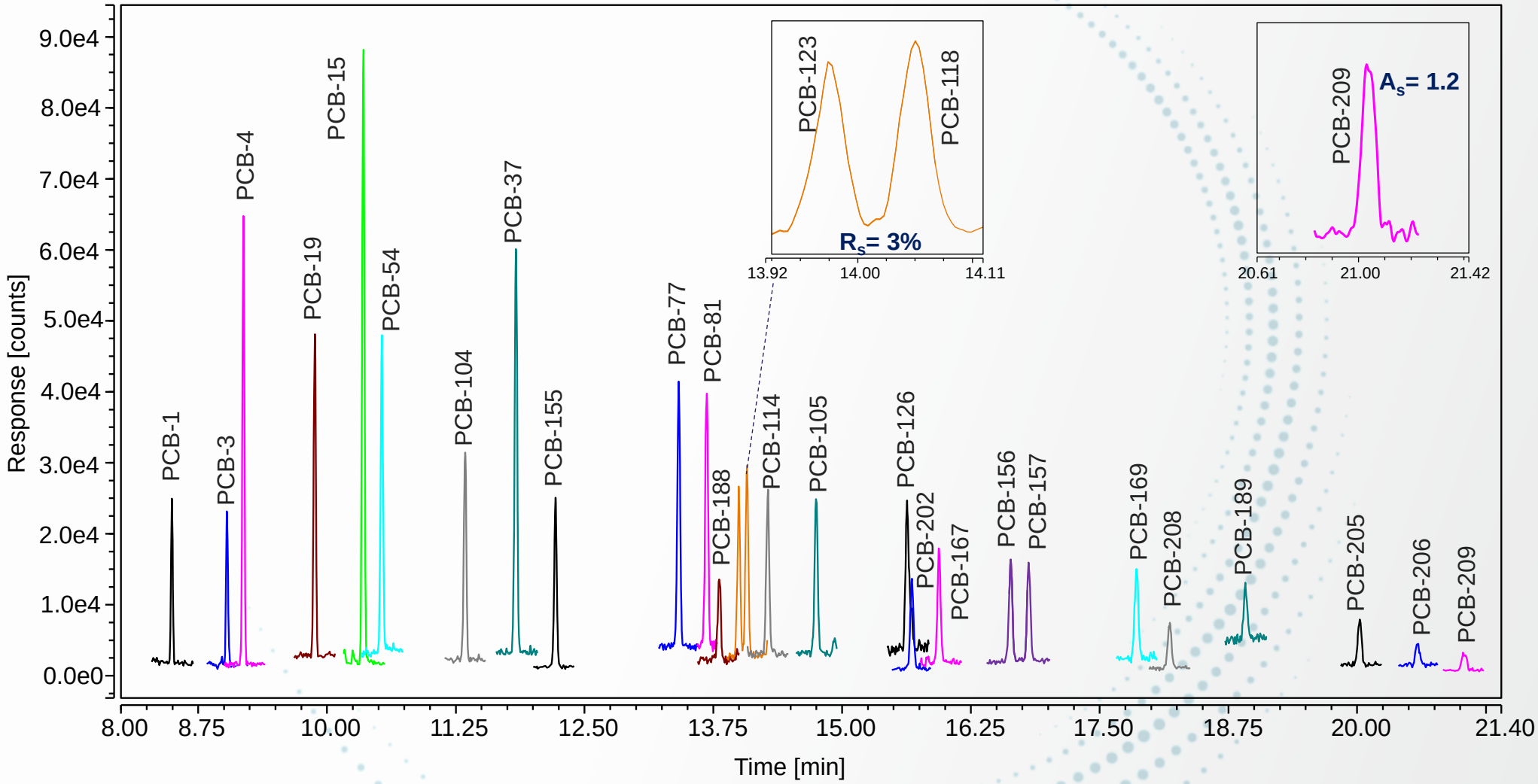
t-SRM for improved selectivity

Compound	Retention time (min)	Precursor Ion (Da)	Product Ion (Da)	Collision Energy (V)
PCB-1	8.5	188.04	153.04	22
PCB-1	8.5	190.04	153.04	22
PCB-1L13C	8.5	200.08	165.10	22
PCB-1L13C	8.5	202.08	165.10	22
PCB-3	9.03	188.04	153.04	22
PCB-3	9.03	190.04	153.04	22
PCB-3L13C	9.03	200.08	165.10	22
PCB-3L13C	9.03	202.08	165.10	22
PCB-4	9.19	222.00	152.06	22
PCB-4	9.19	224.00	152.06	22
PCB-4L13C	9.19	234.04	164.10	22
PCB-4L13C	9.19	236.04	164.10	22
PCB-19	9.88	255.96	186.02	22
PCB-19	9.88	257.96	186.02	22
PCB-19L13C	9.88	268.00	198.02	22
PCB-19L13C	9.88	270.00	198.02	22
PCB-15	10.36	222.00	152.06	22
PCB-15	10.36	224.00	152.06	22
PCB-15L13C	10.36	234.04	164.10	22
PCB-15L13C	10.36	236.04	164.10	22
PCB-54	10.54	289.92	219.98	22
PCB-54	10.54	291.92	219.98	22
PCB-54L13C	10.54	301.96	232.02	22
PCB-54L13C	10.54	303.96	232.02	22
PCB-104	11.34	323.90	253.95	22
PCB-104	11.34	325.90	255.95	22
PCB-104L13C	11.34	335.92	265.99	22
PCB-104L13C	11.34	337.92	267.99	22
PCB-37	11.84	255.96	186.02	22
PCB-37	11.84	257.96	186.02	22
PCB-37L13C	11.84	268.00	198.02	22
PCB-37L13C	11.84	270.00	198.02	22
PCB-155	12.2	357.80	287.90	24
PCB-155	12.2	359.80	289.95	24
PCB-155L13C	12.2	369.90	299.51	24
PCB-155L13C	12.2	371.90	301.95	24
PCB-101L13C	12.59	335.92	265.99	22
PCB-101L13C	12.59	337.92	267.99	22
PCB-111L13C	13.13	335.92	265.99	22
PCB-111L13C	13.13	337.92	267.99	22
PCB-77	13.42	289.92	219.98	22
PCB-77	13.42	291.92	219.98	22
PCB-77L13C	13.42	301.96	232.02	22
PCB-77L13C	13.42	303.96	232.02	22
PCB-81	13.69	289.92	219.98	22
PCB-81	13.69	291.92	219.98	22
PCB-81L13C	13.69	301.96	232.02	22
PCB-81L13C	13.69	303.96	232.02	22
PCB-188	13.8	391.80	321.90	25
PCB-188	13.8	393.80	323.90	25
PCB-188L13C	13.8	403.80	333.90	25
PCB-188L13C	13.8	405.80	335.90	25
PCB-123	13.97	323.90	253.95	22
PCB-123	13.97	325.90	255.95	22
PCB-123L13C	13.97	335.92	265.99	22
PCB-123L13C	13.97	337.92	267.99	22

Compound	Retention time (min)	Precursor Ion (Da)	Product Ion (Da)	Collision Energy (V)
PCB-118	14.05	323.90	253.95	22
PCB-118	14.05	325.90	255.95	22
PCB-118L13C	14.05	335.92	265.99	22
PCB-118L13C	14.05	337.92	267.99	22
PCB-114	14.28	323.90	253.95	22
PCB-114	14.28	325.90	255.95	22
PCB-114L13C	14.28	335.92	265.99	22
PCB-114L13C	14.28	337.92	267.99	22
PCB-105	14.75	323.90	253.95	22
PCB-105	14.75	325.90	255.95	22
PCB-105L13C	14.75	335.92	265.99	22
PCB-105L13C	14.75	337.92	267.99	22
PCB-126	15.64	323.90	253.95	22
PCB-126	15.64	325.90	255.95	22
PCB-126L13C	15.64	335.92	265.99	22
PCB-126L13C	15.64	337.92	267.99	22
PCB-202	15.68	427.80	357.80	25
PCB-202	15.68	429.80	357.80	25
PCB-202L13C	15.68	439.80	369.90	25
PCB-202L13C	15.68	441.80	369.90	25
PCB-167	16	357.80	287.90	24
PCB-167	16	359.80	289.95	24
PCB-167L13C	16	369.90	299.51	24
PCB-167L13C	16	371.90	301.95	24
PCB-156	16.6	357.80	287.90	24
PCB-156	16.6	359.80	289.95	24
PCB-156L13C	16.6	369.90	299.51	24
PCB-156L13C	16.6	371.90	301.95	24
PCB-157	16.82	357.80	287.90	24
PCB-157	16.82	359.80	289.95	24
PCB-157L13C	16.82	369.90	299.51	24
PCB-157L13C	16.82	371.90	301.95	24
PCB-169	17.86	357.80	287.90	24
PCB-169	17.86	359.80	289.95	24
PCB-169L13C	17.86	369.90	299.51	24
PCB-169L13C	17.86	371.90	301.95	24
PCB-208	18.18	461.70	391.80	25
PCB-208	18.18	463.70	393.80	25
PCB-208L13C	18.18	473.80	403.80	25
PCB-208L13C	18.18	475.80	405.80	25
PCB-189	18.92	391.80	321.90	25
PCB-189	18.92	393.80	323.90	25
PCB-189L13C	18.92	403.80	333.90	25
PCB-189L13C	18.92	405.80	335.90	25
PCB-205	20.04	427.80	357.80	25
PCB-205	20.04	429.80	357.80	25
PCB-205L13C	20.04	439.80	369.90	25
PCB-205L13C	20.04	441.80	369.90	25
PCB-206	20.6	461.70	391.80	25
PCB-206	20.6	463.70	393.80	25
PCB-206L13C	20.6	473.80	403.80	25
PCB-206L13C	20.6	475.80	405.80	25
PCB-209	21.03	495.70	425.80	25
PCB-209	21.03	497.70	427.80	25
PCB-209L13C	21.03	507.70	437.80	25
PCB-209L13C	21.03	509.70	439.80	25



Chromatographic resolution of critical pairs



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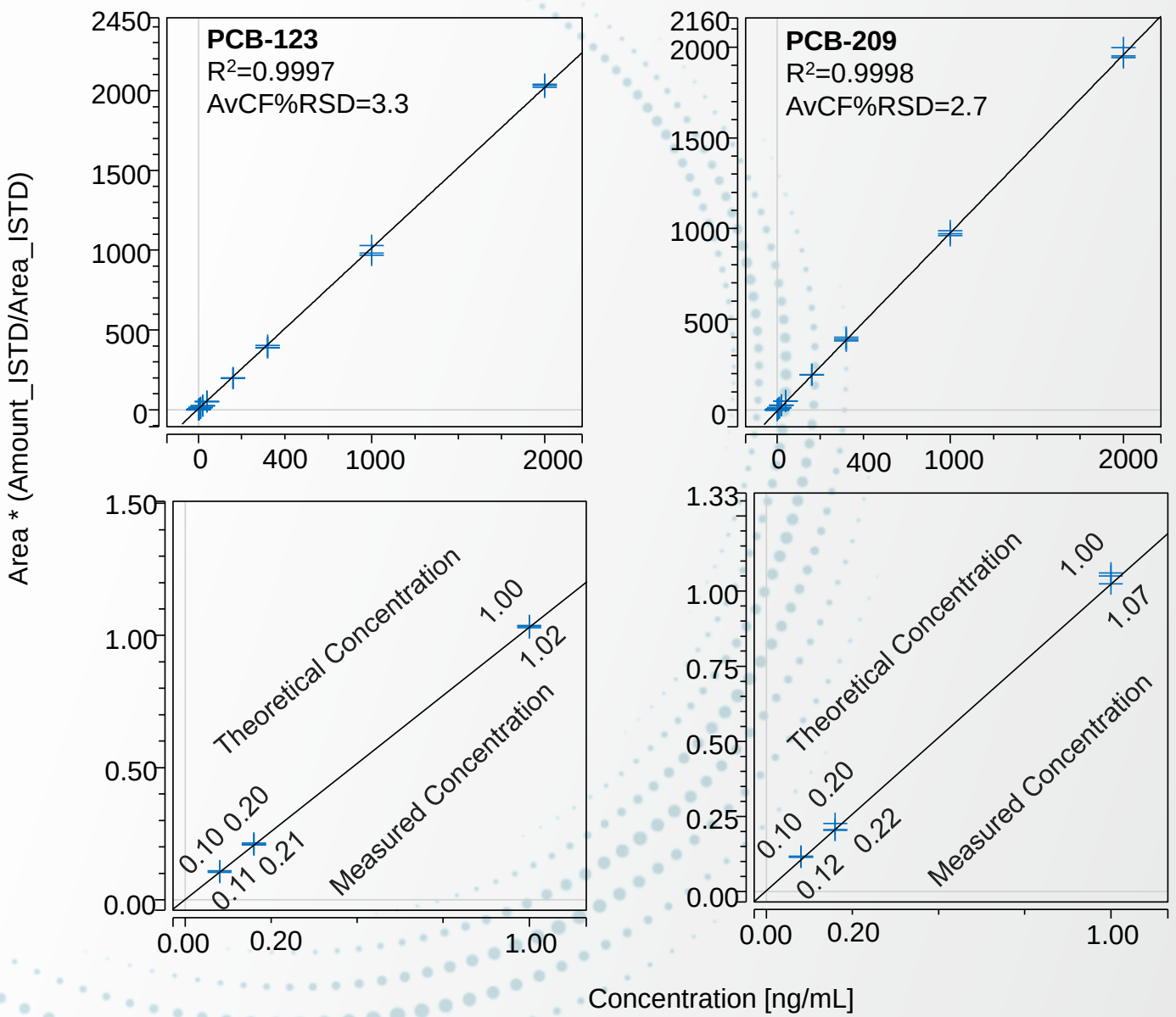
Linearity for accurate quantitative analysis

Compound	Retention Time (min)	Coefficient of determination (R^2)	AvCF %RSD
PCB-1	8.49	0.99993	1.5
PCB-3	9.03	0.99996	1.2
PCB-4	9.19	0.99987	2.1
PCB-19	9.88	0.99992	1.6
PCB-15	10.35	0.99996	1.2
PCB-54	10.53	0.99987	2.1
PCB-104	11.34	0.99987	2.1
PCB-37	11.83	0.99989	1.9
PCB-155	12.21	0.99168	17.3
PCB-77	13.40	0.99956	3.9
PCB-81	13.68	0.99925	5.0
PCB-188	13.80	0.99974	2.9
PCB-123	13.96	0.99967	3.3
PCB-118	14.04	0.99972	3.1
PCB-114	14.27	0.99962	3.6
PCB-105	14.74	0.99969	3.2
PCB-126	15.62	0.99990	1.9
PCB-202	15.67	0.99977	2.7
PCB-167	15.93	0.99707	10.0
PCB-156	16.62	0.99473	13.8
PCB-157	16.80	0.99437	14.3
PCB-169	17.84	0.99434	14.4
PCB-208	18.16	0.99991	1.8
PCB-189	18.90	0.99979	2.6
PCB-205	20.00	0.99960	3.6
PCB-206	20.57	0.99989	1.9
PCB-209	21.02	0.99978	2.7



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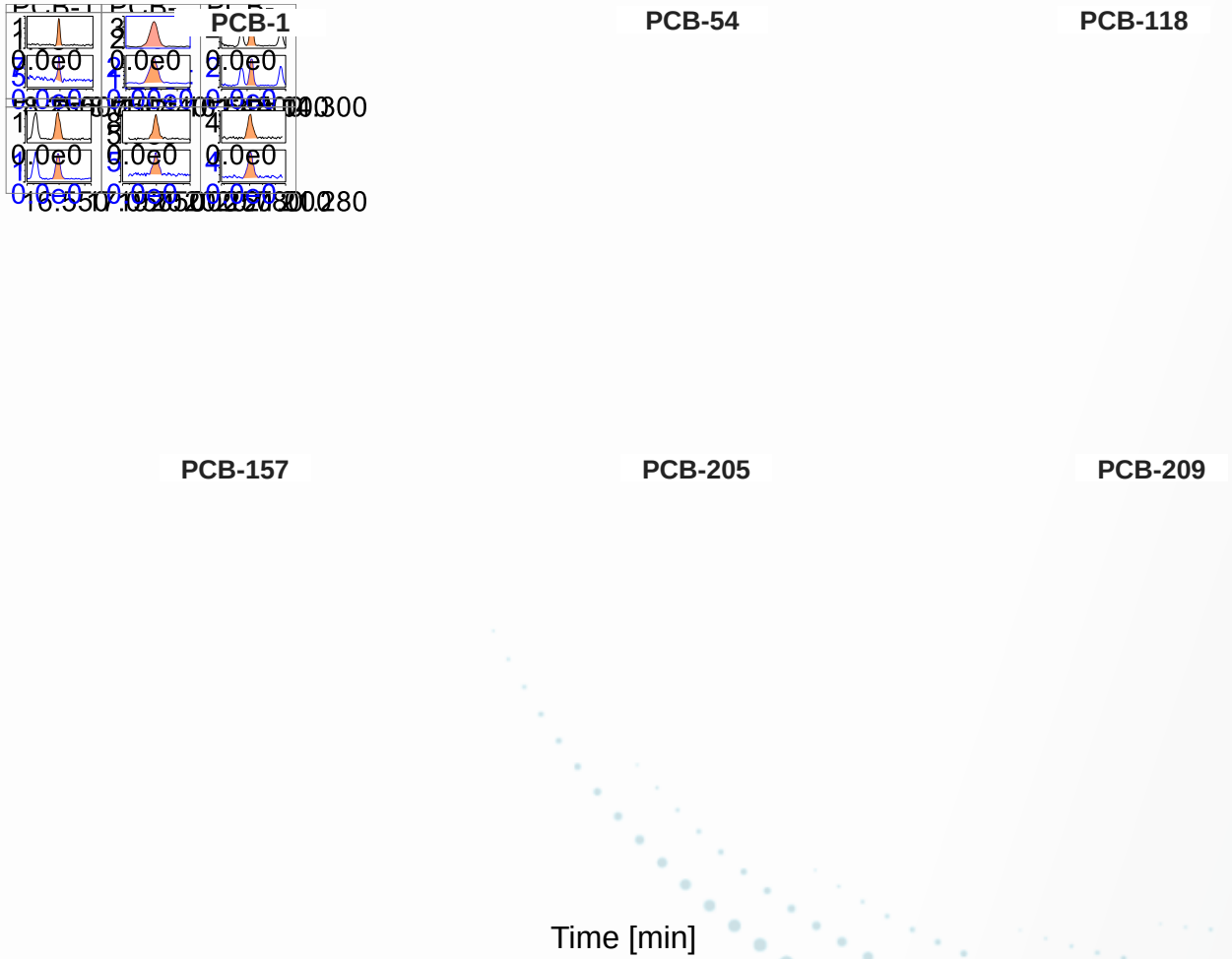
Assessment of Sensitivity

LOQ = 0.05 ng/mL

(i) ion ratios within ± 15% the expected values

(ii) absolute peak area RSD <15%

(iii) the response factor (RF) RSD <15%



Compound	Absolute Peak Area %RSD (n=10)	RF %RSD	Expected IR	Average Measured IR (n=10)	Calculated IDL (fg OC)
PCB-1	2.2	2.4	33	33	3
PCB-3	4.1	4.3	33	35	6
PCB-4	5.4	5.2	64	65	8
PCB-19	2.8	2.9	62	67	4
PCB-15	2.9	2.3	64	67	4
PCB-54	1.8	2.8	64	65	3
PCB-104	7.3	6.3	95	99	10
PCB-37	2.4	2.4	61	63	3
PCB-155	13.5	6.5	124	123	19
PCB-77	3.0	1.9	63	66	4
PCB-81	3.1	2.9	63	65	4
PCB-188	6.4	6.2	157	148	9
PCB-123	7.5	7.5	102	94	11
PCB-118	4.1	3.5	101	96	6
PCB-114	4.9	4.1	96	97	7
PCB-105	4.8	5.7	95	93	7
PCB-126	13.0	11.6	90	83	18
PCB-202	5.4	6.6	64	66	8
PCB-167	4.8	5.3	123	119	7
PCB-156	10.5	8.2	123	130	15
PCB-157	9.1	5.4	122	128	13
PCB-169	5.9	10.4	129	132	8
PCB-208	9.9	6.6	98	98	14
PCB-189	11.2	10.9	154	151	16
PCB-205	8.0	6.4	64	64	11
PCB-206	8.8	6.2	97	98	12
PCB-209	8.8	6.6	110	111	12

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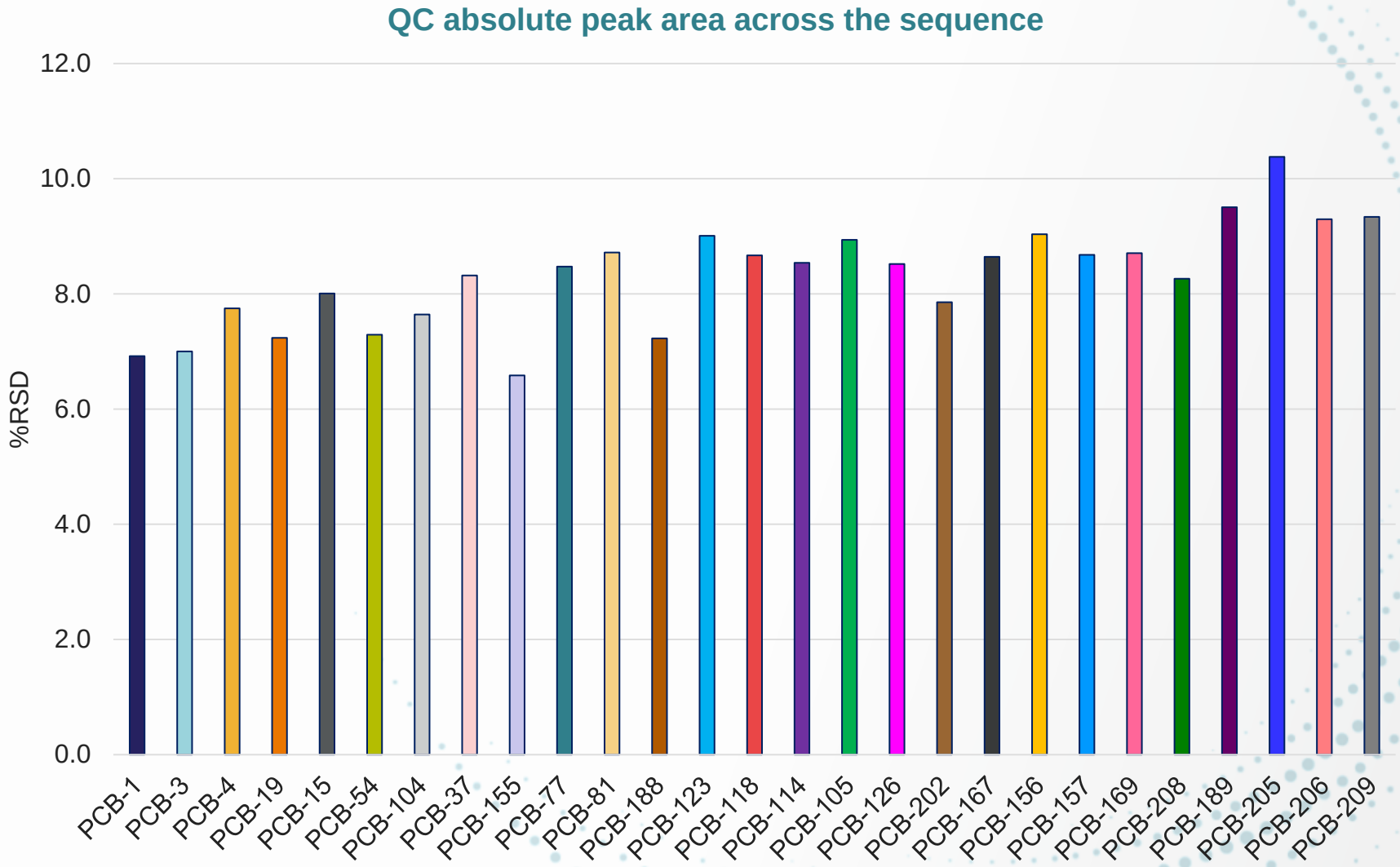
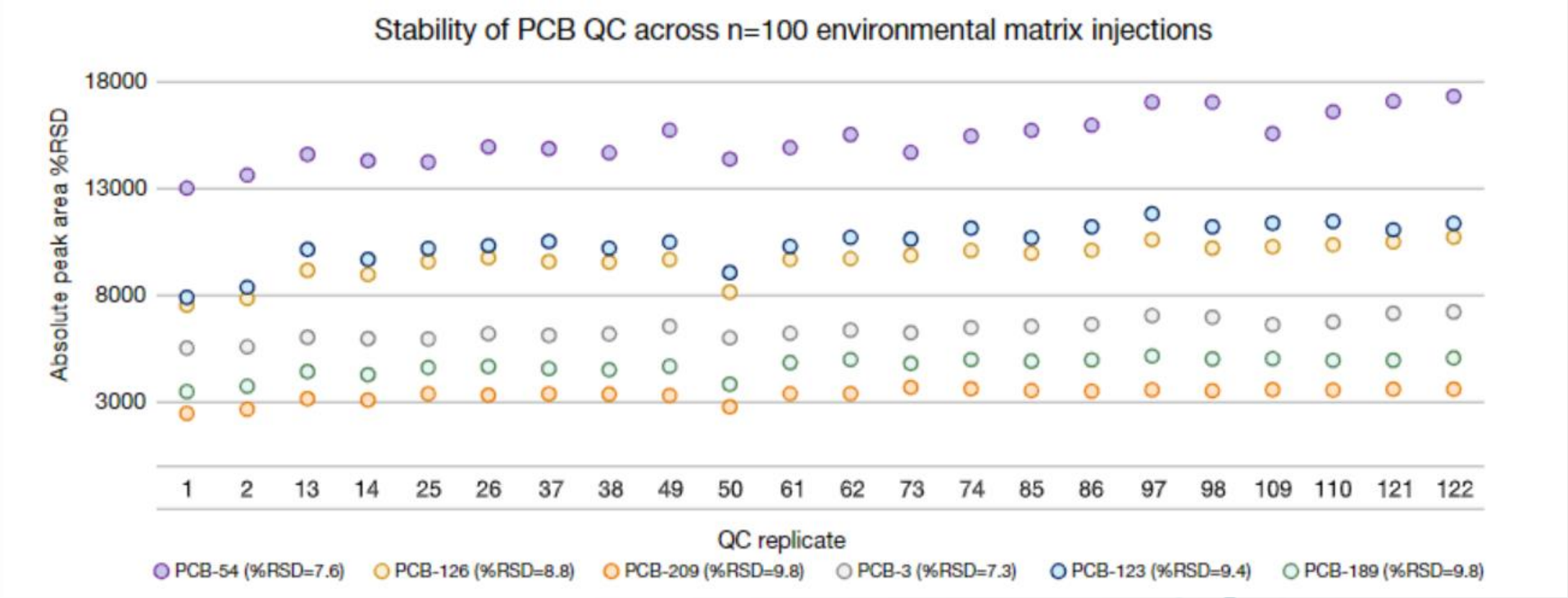
Reproducibility



Compound	QC absolute peak area %RSD
PCB-1	6.9
PCB-3	7.0
PCB-4	7.7
PCB-19	7.2
PCB-15	8.0
PCB-54	7.3
PCB-104	7.6
PCB-37	8.3
PCB-155	6.6
PCB-77	8.5
PCB-81	8.7
PCB-188	7.2
PCB-123	9.0
PCB-118	8.7
PCB-114	8.5
PCB-105	8.9
PCB-126	8.5
PCB-202	7.9
PCB-167	8.6
PCB-156	9.0
PCB-157	8.7
PCB-169	8.7
PCB-208	8.3
PCB-189	9.5
PCB-205	10.4
PCB-206	9.3
PCB-209	9.3

Reproducibility



Conclusions

- The TRACE TR-PCB column ensured chromatographic separation of the target analytes in about 21 minutes with calculated resolution of the critical pair PCB-123 / PBDE-118 of 3%.
- The column thin film phase, high thermal stability, and low column bleed ensured elution of the high boiling point PCBs (e.g., PCB-209) with improved peak shapes.
- We demonstrated linearity over a concentration range of 0.10 to 2,000 ng/mL with coefficient of determination of R^2 >0.990 and AvCF %RSDs <20.
- IDLs ranged from 3 fg to 19 fg OC (corresponding to 0.15 pg/L to 0.95 pg/L in water samples and to 0.015 to 0.095 ng/kg in soil samples) and LOQ set at 0.05 ng/mL.
- Extended robustness demonstrated over 100 injections without need for maintenance or re-tuning.


Thank you