Certified Reference Materials (CRMs) for the Analysis of Persistent Organic Pollutants (POPs) in Environmental Samples

(An Analytical Chemist's Perspective)

What is a Persistent Organic Pollutant?

UNEP (United Nations Environmental Programme) definition of POP:

- Chemical Substances that persist in the Environment
- Bioaccumulate through the food web
- Pose a risk of causing adverse affects to human health
- Evidence of long range transport to regions where they have never been used

POPs in Environmental Samples: The Analytical Challenge

- Millions of organic chemicals
  - **There are 45 million compounds listed in ChemSpider - WWW.Chemspider.com**
- Many congeners per analyte group

  [dioxins/furans: 210; PCBs: 209, Toxaphene: >600]
- Separate and accurately quantify all toxic congeners

  [dioxins/furans: 17, PCBs: 12, Toxaphene: 5]
- Toxicity can range up to 6 orders of magnitude

  [NOEL = 3g/kg to LD_{50} = 1 ug/kg]
- Wide range of concentrations [fg/g (10^{-15}g/g) to %]
- Range of sample types, complexities

  [biota, air, water, soil, haz. waste, other]

TCDD: 2,3,7,8-tetrachlorodibenzo-p-dioxin
NOEL: No-observable effect-level
LD_{50}: Lethal dose (50% test population)

Ontario

POPs in Environmental Samples: The Analytical Challenge

- Quantitatively extract analytes from matrix
- Extract may contain up to 1 gram of co-extractable organic material
  - polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organochlorine pesticides (OCs), brominated flame retardants (BFRs), polychlorinated naphthalenes (PCNs), polychlorinated diphenyl ethers (PCDEs)
- Extract must be cleaned to remove interfering co-extractables
- Separate target analytes from non-target isomers or congeners
- Detect analytes at sub picogram level – for dioxin every piece of labware should be prechecked to contain less than 0.5 pg
- Ensure instrument selectivity and sensitivity to meet data quality objectives (DQOs) – Limit of Detection, Limit of Quantification
- Ensure quantitative accuracy (CRMs, ILS, External Standards)

Environ. Sci. Technol. 2006, 40, 7157–7166

Are There Other Persistent Organic Pollutants? A Challenge for Environmental Chemists†

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Environ. Sci. Technol. 2010, 44, 2277–2285

Identifying New Persistent and Bioaccumulative Organics Among Chemicals in Commerce

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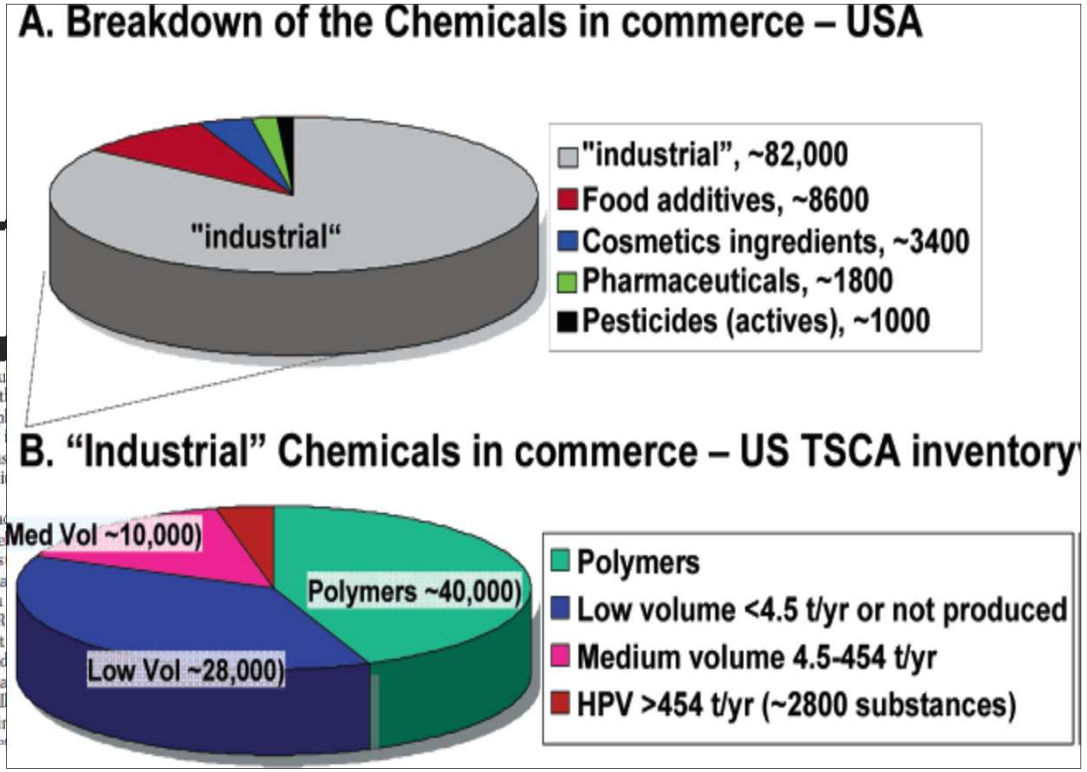
Contamination and Bioaccumu
This database of chemicals in t
mercial chemicals, pesticides, p
tives, and chemicals detected
matched these chemicals agains
ume (HPV) chemical lists to i
chemicals.

This ability to screen thousan
possible because of the deve
Structure Property Relationships
of large chemical structural data
our 2006 article, there still is a
review of the results from QSPR
available QSPRs generally do not
that rapidly degrade (e.g., peroxid
groups). Also, chemicals that a
intermediates need to be carefull
they will be released to the envi
consideration of chemical prope

A. Breakdown of the Chemicals in commerce – USA



B. "Industrial" Chemicals in commerce – US TSCA inventory

Atmospheric Pollution Research
www.atmospolres.com

How many persistent organic pollutants should we expect?

Martin Scheringer [1], Sebastian Strempel [1], Sirja Hukari [1], Carla A. Ng [1], Markus Blepp [2], Konrad Hungerbuhler [1]

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"Beyond these well-known substances, we find 510 chemicals that exceed all four criteria and can be considered potential POPs : Ninety eight percent of these chemicals are halogenated"

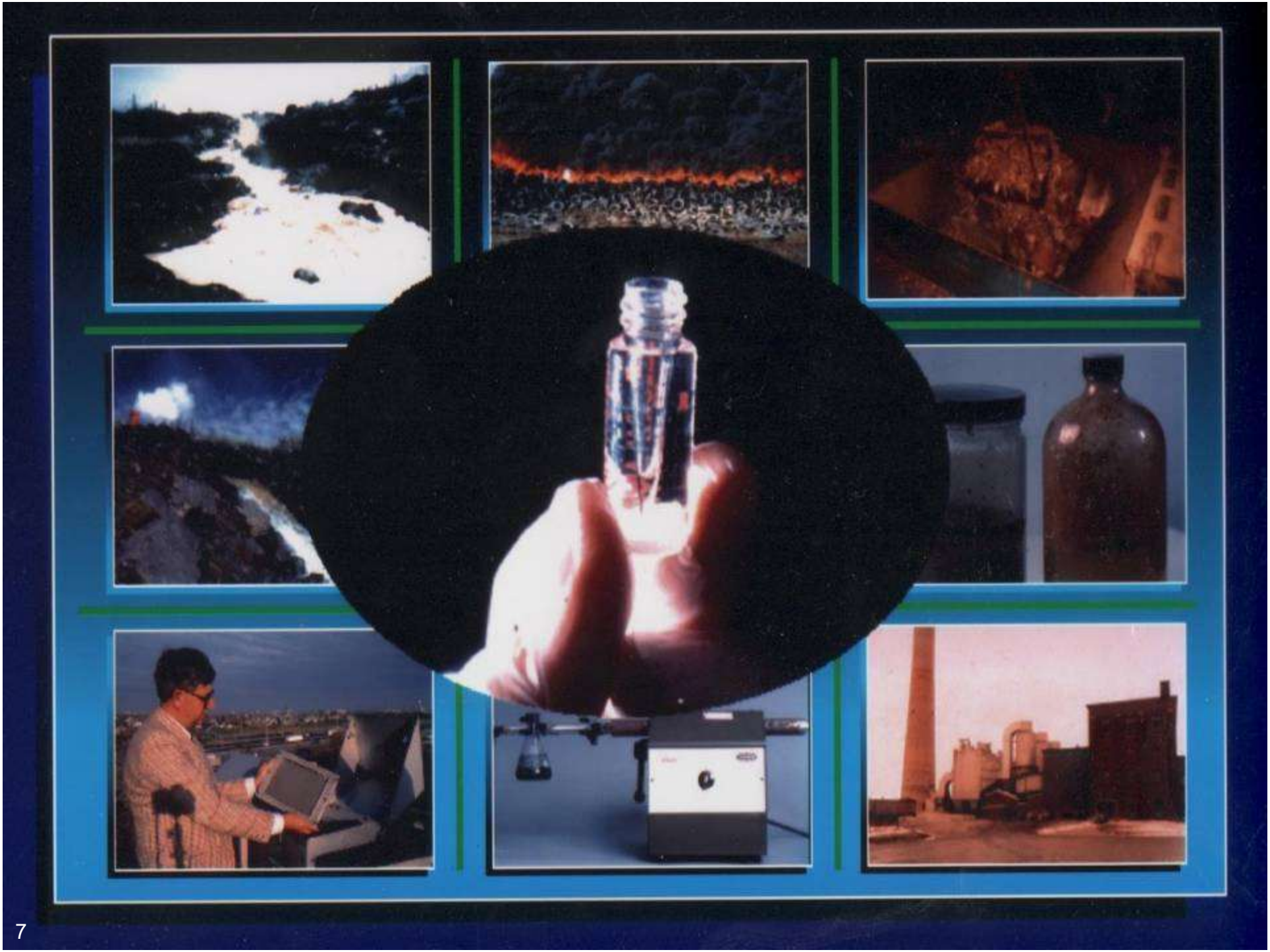
Ontario

Stockholm Agreement Compounds

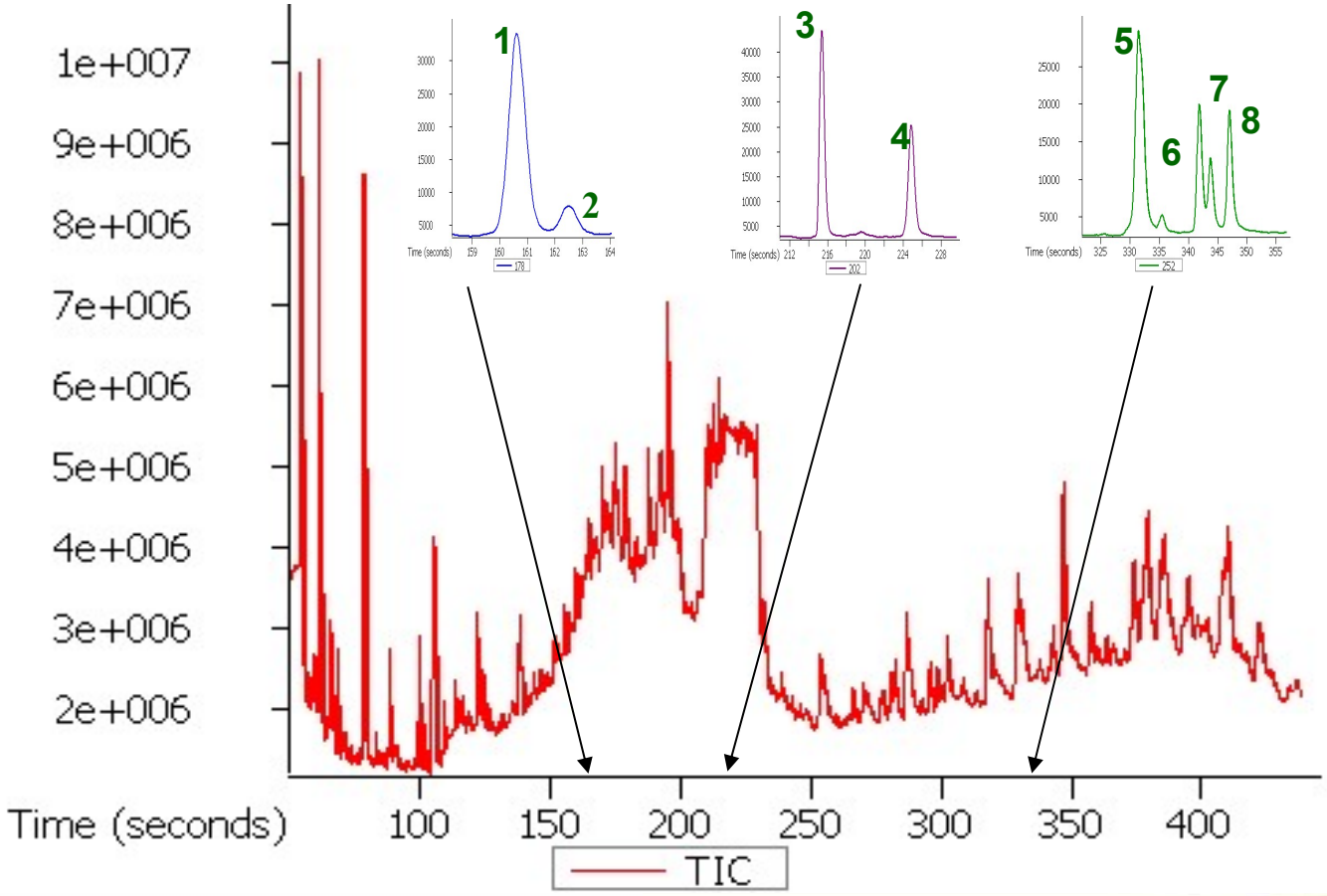
Only a small number are monitored or regulated globally

Original 12	Additional compounds	Under Discussion
aldrin, chlordane, dieldrin, DDT, endrin, heptachlor, hexachlorobenzene (HCB), mirex, toxaphene, polychlorinated biphenyls (PCBs), polychlorinated dibenzodioxins (PCDD) and dibenzofurans (PCDF)	**Added 2009**: chlordecone, α-hexachlorocyclohexane, β-hexachlorocyclohexane, hexabromobiphenyl, tetra- to hepta-bromodiphenylether, lindane (δ-hexachlorocyclohexane), pentachlorobenzene, perfluoroctanesulfonic acid (PFOS), its salts and perfluoroctanesulfonyl fluoride **Added 2011:** endosulfan, **Added 2013:** hexabromocyclododecane (HBCD)	short chain chlorinated paraffins (SCCPs),

Ontario



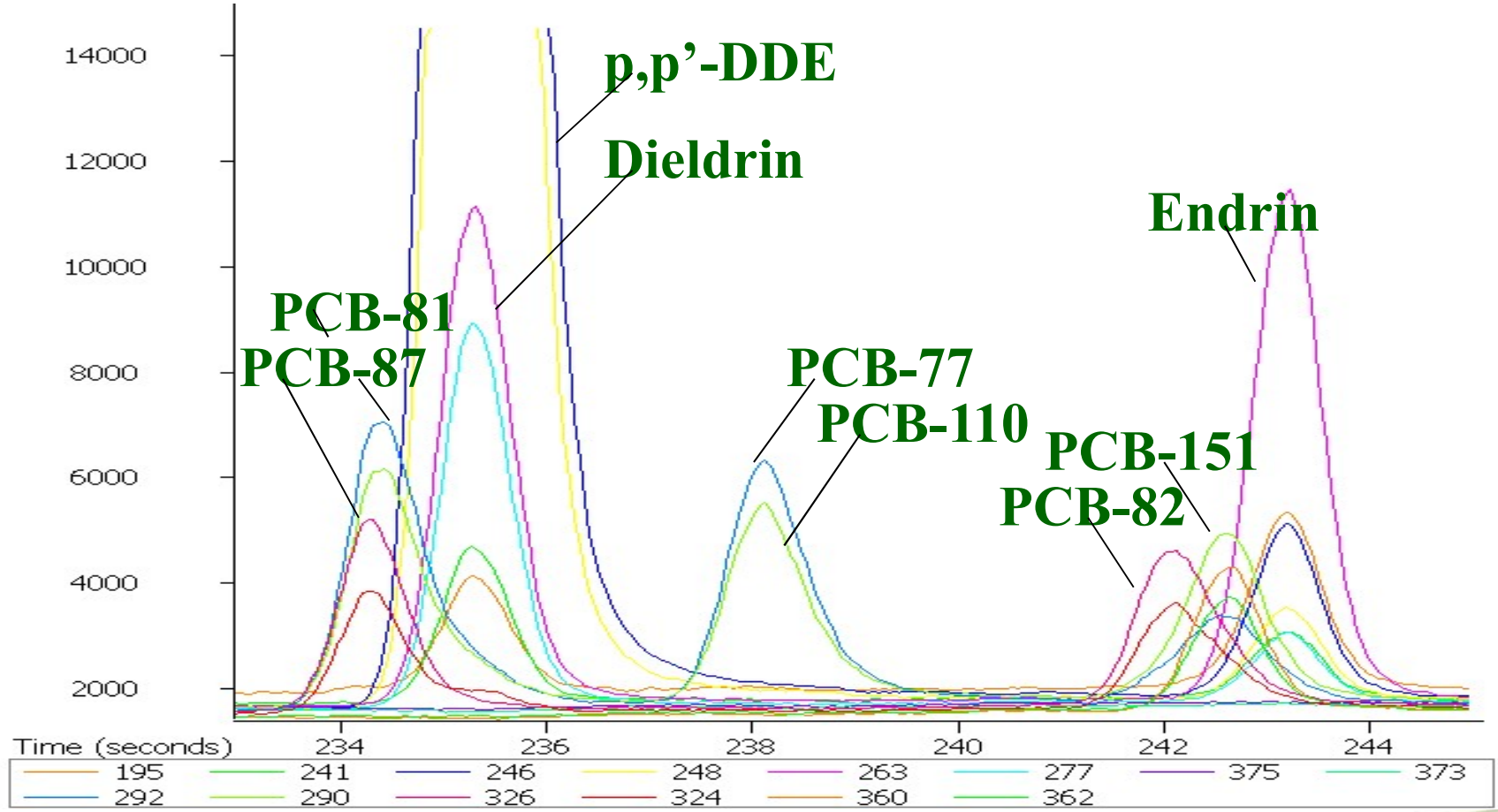
Sediment - Target Compounds



1. Phenanthrene
2. Anthracene
3. Fluoranthene
4. Pyrene
5. Benzofluoranthenes
6. Benzo[e]pyrene
7. Benzo[a]pyrene
8. Perylene

Ontario

Other Target Compounds



Standard targeted methods are adept at “finding a needle in a haystack”

Challenges for Non-Targeted Analysis

- Is the extraction method quantitative?
- Are compounds lost in the sample preparation or concentration procedure?
- Is the instrument able to detect compounds without significant bias?
- Are standards available?

Identifying Unknown Compounds

- Compounds must be separated from bulk matrix and other interfering compounds or isomers – GC, GCxGC or LC is used to **attempt to get a clean mass spectrum**
- Use tandem mass spectrometry (MS/MS) or high resolution mass Spectrometry (HRMS) to confirm elemental composition, structure and functional groups
- Requires extensive investigative work – background knowledge from patents, manufacturers, e.g. INCHEM (International Programme on Chemical Safety – www.inchem.org, ChemSpider, www.chemspider.com.
- If not available, must have some prior knowledge of the compounds structure or functional groups to interpret mass chromatograms and spectra
- Synthesize compound as authentic standard for confirmation

Identification of Unknowns

- Target Compound Analysis
  - Stockholm POPs, PCNs, PAH, PCPPs – Established methods, optimized for target compounds – Very specific and can filter out any potential unknowns
- Suspect Targeted Identification
  - Compounds in Industrial Products, Patents Howard & Muir EST 2010 (>500 compounds)
  - Have some information to help find compounds
- Untargeted Unknowns
  - Other compounds and degradation products

Unknown ID Tool Kit

Use selective detection:

- Advanced chromatography – GCxGC, Scripting
- Advanced Mass Spectrometry – HRMS, MS/MS (parent, daughter, neutral loss scans), FTICRMS

No previous information

- identify by first principals
  - RDBE, Element Restriction Rule, Nitrogen Rule, LEWIS and SENIOR (valence) Rules, Isotope Patterns, H/C check, Hetroatom/Carbon (<1.3) and data bases (CAS, ChemSpider)

Kind et al, BMC Bioimformatics, (2007), 8, 105
Godfrey et al, Anal Bioanal Chem, (2012) 404, 1159

ISO/IEC 17025:2005

General requirements for the competence of testing and calibration laboratories

- A standard that specifies the general requirements for laboratory competence to carry out tests and/or calibrations, including sampling and testing and calibration performed using standard methods, non-standard methods, and laboratory-developed methods.
- Laboratories in most jurisdictions must be accredited to this standard.
- It is applicable to all organizations performing tests and/or calibrations regardless of the extent of the scope of testing and/or calibration activities

Ontario

ISO/IEC 17025:2005

- Laboratories are accredited using a third party review process.
- Accreditation involves a thorough evaluation of the laboratory's quality management system on a regular basis to ensure continued technical competence and compliance with ISO/IEC 17025.
- Laboratory accreditation can only be granted by an accreditation body, e.g A2LA, CALA,

Ontario

ISO/IEC 17025:2005

- The quality management system includes a series of documents: standard operation procedures, analytical methods, **documentation for method and analyst training and performance, calibration and traceability**.
- **Certified standards and certified reference materials** are tools for the determination and assessment of the level of quality of the results being produced by the laboratory.

Ontario

Uses of CRMs

ISO Guide 33

- Calibration of equipment or a measurement procedure
- Establishing metrological tractability
- Method validation
- Assigning values to other materials (eg. validating standards)
- Quality control of a measurement or measurement procedure
- Maintaining conventional scales (eg. pH, Octane number)

Ontario

Challenges for POPs CRM production

- Candidate materials have few analytes or are contaminated by one group
- Very few materials have all analytes that are fit for purpose
- Candidate samples are often not homogeneous
- May require review of many samples to find a candidate RM
- Contaminated samples can contain interferences that result in bias

Ontario

Production of CRMs for POPs

- Find potential RM candidates
  - Can be challenging for POPs
- Obtain material for processing
- Initial processing
  - Freeze drying, grinding, sifting, homogenization
- Assess initial levels of analytes
  - Targeted and non-targeted analytes
  - Assess potential interferences
- Determine initial homogeneity
  - Use organic carbon (soil sediment) or lipid (biota)
- Re-homoginize (if necessary)

Ontario

Production of CRMs for POPs

- Package samples in appropriate containers
- Obtain analytical results for analytes
  - Use Interlab study and/or orthogonal methods e.g. GC-MS vs GCxGC-ECD
- Reassess homogeneity of RM
  - Assess within bottle vs between bottle homogeneity
- Determine stability of reference analytes
- Determine reference values and uncertainties
- Develop certificates

Ontario

A sediment RM for POPs analysis WMS-01

- Bay of Quinte is a depositional area of the Trent river
- Replicate sample analysis showed excellent homogeneity of sediment with low dioxin levels.
- CRM contains 2,3,7,8-PCDD/Fs and Dioxin-like PCBs at levels lower than most CRMs
- The Canadian Centre for Mineral and Energy Technology (CANMET), certified to ISO 9002 performed the physical processing of the sediment.

Ontario

A sediment RM for POPs analysis
WMS-01

Processing stages included:

a) air drying at room temperature;

b) crushing to break the agglomerates;

c) further air drying at room temperature;

d) initial sieving through a 1.40 mm (14 mesh) screen;

e) sieving the < 1.40 mm fraction through a 75 µm (200 mesh) screen;

f) grinding of all < 1.40 mm and > 75 µm fractions;

g) resieving the ground material through the 75 µm screen;

Ontario

A sediment CRM for POPs analysis
WMS-01

Processing stages included (cont'd):

h) regrinding the > 75 µm fraction;

i) sieving the re-ground material through the 75 µm screen;

j) blending the three fractions of < 75 µm mesh material;

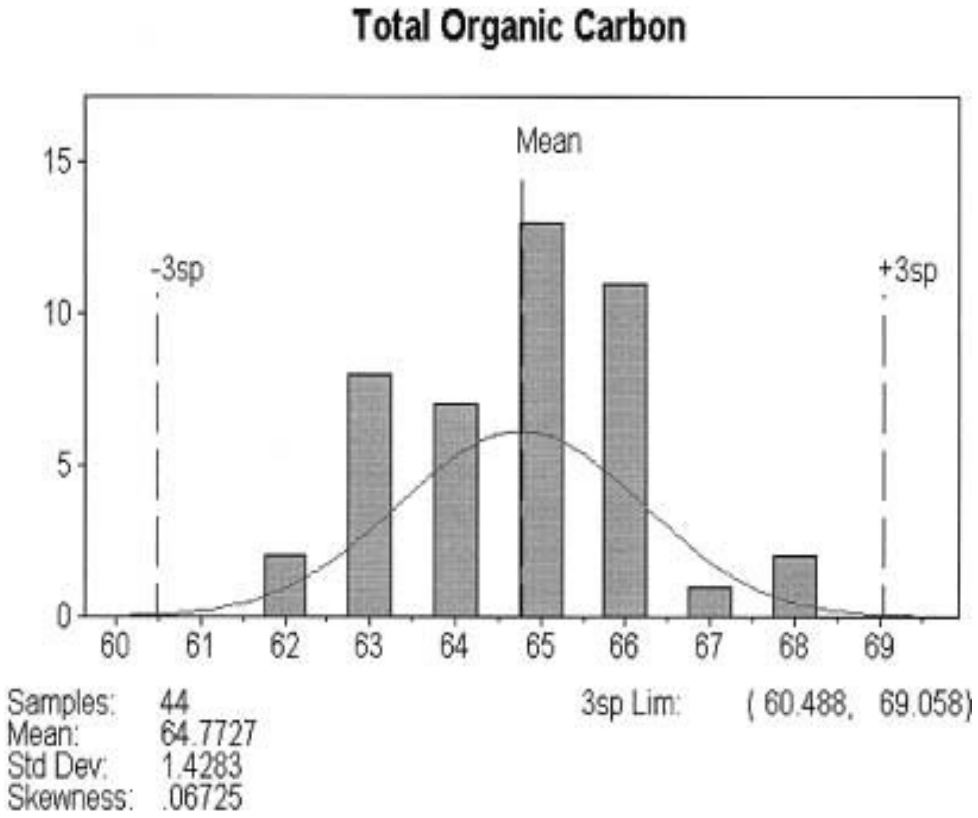
k) bottling the material in 25 g aliquots; and

l) labeling.

A total of 1200 × 25 g bottles were produced.

Ontario

A sediment RM for POPs analysis
WMS-01

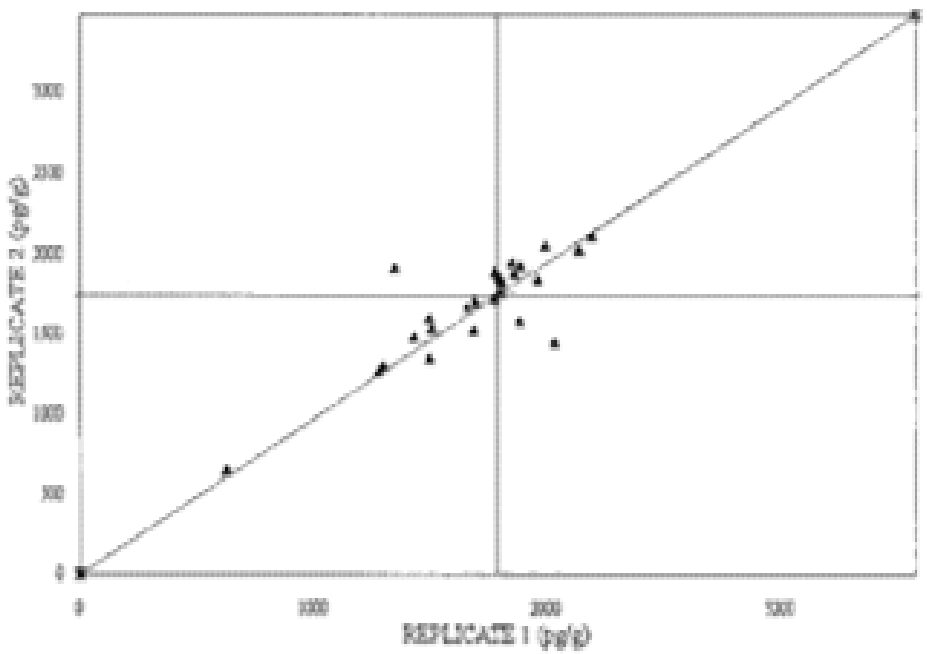


The results 15 metals and bromine, were used to determine homogenetity. Of the 44 results, only 6 differed by more than 5% from the mean, and all differed by less than 8% from the mean. Using ANOVA, the ratio of between-bottle to within-bottle mean squares *(F calculated)* was compared to the *F Statistic at the 95% confidence* level.

For all elements listed above, the *F calculated was* less than the *F Table values, indicating there was no evidence* of inhomogeneity.

Ontario

A sediment RM for POPs analysis
WMS-01



Youden Plot for PCB-77
SAMPLE 1 vs. SAMPLE 2

The K-S procedure (a modified form of the Youden procedure) was applied to each analyte to estimate the average within laboratory standard deviation. The results were plotted Replicate 1 vs Replicate 2 . The graph is divided into four quadrants . The data points represent a pair of data from each laboratory. The majority of the results were either in the lower left quadrant or in the upper right quadrant, very close to the 45 degree line. This demonstrates that most laboratories were capable of precise, but not always accurate analysis. It also confirms the CRM was homogeneous.

Ontario

WMS-01

Parameter	Assigned value and uncertainty	N	Coefficient of Variation
2,3,7,8-TCDD	17.7 ± 5.6	69	15.8%
1,2,3,7,8-PeCDD	7.96 ± 2.8	67	17.7%
1,2,3,4,7,8-HxCDD	8.66 ± 2.7	62	15.6%
1,2,3,6,7,8-HxCDD	20.8 ± 4.8	62	11.8%
1,2,3,7,8,9-HxCDD	17.3 ± 8.0	66	22.9%
1,2,3,4,6,7,8-HpCDD	293 ± 63	66	10.7%
1,2,3,4,6,7,8,9-OCDD	1899 ± 456	69	12.0%
2,3,7,8-TCDF	52.5 ± 16	31	15.0%
1,2,3,7,8-PeCDF	12.6 ± 5	65	19.9%
2,3,4,7,8-PeCDF	18.5 ± 6	61	16.6%
1,2,3,4,7,8-HxCDF	67.3 ± 24	66	17.8%
1,2,3,6,7,8-HxCDF	20.3 ± 8.7	64	22.0%
1,2,3,7,8,9-HxCDF	2.68a ± 4.0	44	74.0%
2,3,4,6,7,8-HxCDF	16 ± 8	63	25.0%
1,2,3,4,6,7,8-HpCDF	299 ± 73	68	12.2%
1,2,3,4,7,8,9-HpCDF	15.1 ± 4.6	64	15.1%
1,2,3,4,6,7,8,9-OCDF	509 ± 157	65	15.4%

Results in pg/g

WMS-01

Parameter	Assigned value and uncertainty	N	Coefficient of Variation
PCB-077 (3,3',4,4'-TCB)	1717 ± 520	26	15.0%
PCB-081 (3,4,4',5-TCB)	75 ± 79	22	53.0%
PCB-105 (2,3,3',4,4'-PeCB)	3998 ± 951	48	12.0%
PCB-114 (2,3,4,4',5-PeCB)	207 ± 128	46	31.0%
PCB-118 (2,3',4,4',5-PeCB)	8115 ± 1663	42	10.0%
PCB-123 (2',3,4,4',5-PeCB)	209 ± 191	41	48.0%
PCB-126 (3,3',4,4',5-PeCB)	84.9 ± 35	43	21.0%
PCB-156 (2,3,3',4,4',5-HxCB)	715 ± 248	51	17.0%
PCB-157 (2,3,3',4,4',5'-HxCB)	186 ± 81	49	22.0%
PCB-167 (2,3',4,4',5,5'-HxCB)	330 ± 85	36	13.0%
PCB-169 (3,3',4,4',5,5'-HxCB)	7.97 ± 5.3	42	33.0%
PCB-189 (2,3,3',4,4',5,5'-HpCB)	85.2 ± 17.8	36	10.0%

Results in pg/g

Ontario

Sediment CRM comparison

Parameter	WMS-01	DX1 (EC2)	DX2 (EC3)	NIST 1944	BCR 530	BCR 529
2,3,7,8-TCDD	17.7	263	262	133		4500
1,2,3,7,8-PeCDD	7.96	22	28	19		440
1,2,3,4,7,8-HxCDD	8.66	23	25	26		1200
1,2,3,6,7,8-HxCDD	20.8	77	85	56	61	5400
1,2,3,7,8,9-HxCDD	17.3	53	58	53	22	3000
1,2,3,4,6,7,8-HpCDD	293	634	757	800		
1,2,3,4,6,7,8,9-OCDD	1899	3932	4402	5800		
2,3,7,8-TCDF	52.5	89	134	39	240	780
1,2,3,7,8-PeCDF	12.6	39	46	45	620	140
2,3,4,7,8-PeCDF	18	62	88	45	321	360
1,2,3,4,7,8-HxCDF	67.3	713	825	220	190	3400
1,2,3,6,7,8-HxCDF	20.3	116	153	90	126	1090
1,2,3,7,8,9-HxCDF	2.68	28	36	19		22
2,3,4,6,7,8-HxCDF	16	57	70	54		370
1,2,3,4,6,7,8-HpCDF	299	2397	3064	1000		
1,2,3,4,7,8,9-HpCDF	15.1	137	152	40		
1,2,3,4,6,7,8,9-OCDF	509	7122	7830	1000		

Results in pg/g

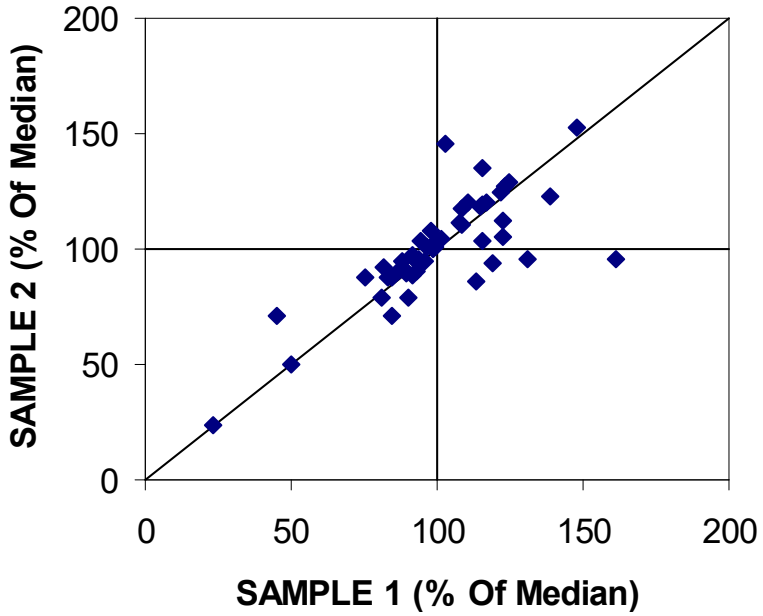
Ontario

A Fish RM for POPs analysis
WMF-01

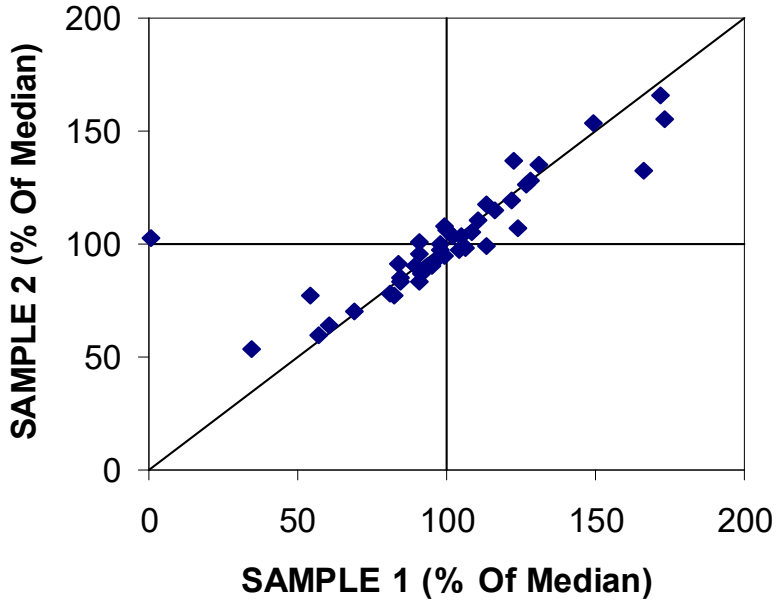
- Four year old Chinook salmon from the Credit river, a tributary of Lake Ontario were collected
- Over 250 kg of fish were collected, filleted and freeze dried to constant weight.
- The freeze dried material was sieved using a 2 mm mesh to remove large cartilaginous materials and blended in a V blender for 16 hours
- The bulk material was tested for lipid levels and 18 PCB congeners to determine homogeneity

Ontario

A sediment RM for POPs analysis
WMF-01



Youden Plot for 2,3,7,8-TCDD
SAMPLE 1 vs. SAMPLE 2



Youden Plot for PCB-77
SAMPLE 1 vs. SAMPLE 2

Ontario

Fish CRM PCB/PBDE comparison

Congener (IUPAC No.)	WMF -01	NRC Carp-2	BCR 682	BCR 718	SRM 1945	SRM 1946	SRM 1947	SRM 1974b	SRM 2977
PCB 77	2.31					0.327			
PCB 81	0.24								
PCB 105	49.7	53.2		0.63	30.1	19.9		39.5	3.76
PCB 114	3.60								
PCB 118	132	148	2.6	1.78	74.6	52.1		102	10.5
PCB 123	6.90								
PCB 126	0.75					0.380			
PCB 156	14.8			0.19	10.3	9.52		7.09	0.960
PCB 157	3.55							0.236	
PCB 167	10.7								
PCB 169	0.079					0.106			
PCB 189	2.01								
BDE 28	3.36					0.742	2.26		
BDE 47	126					29.9	73.3		
BDE 99	41.3					18.5	19.2		
BDE 100	37.2					8.57	17.1		
BDE 153	17					2.81	3.83		
BDE 154	24					5.77	6.88		
BDE 183	0.56								

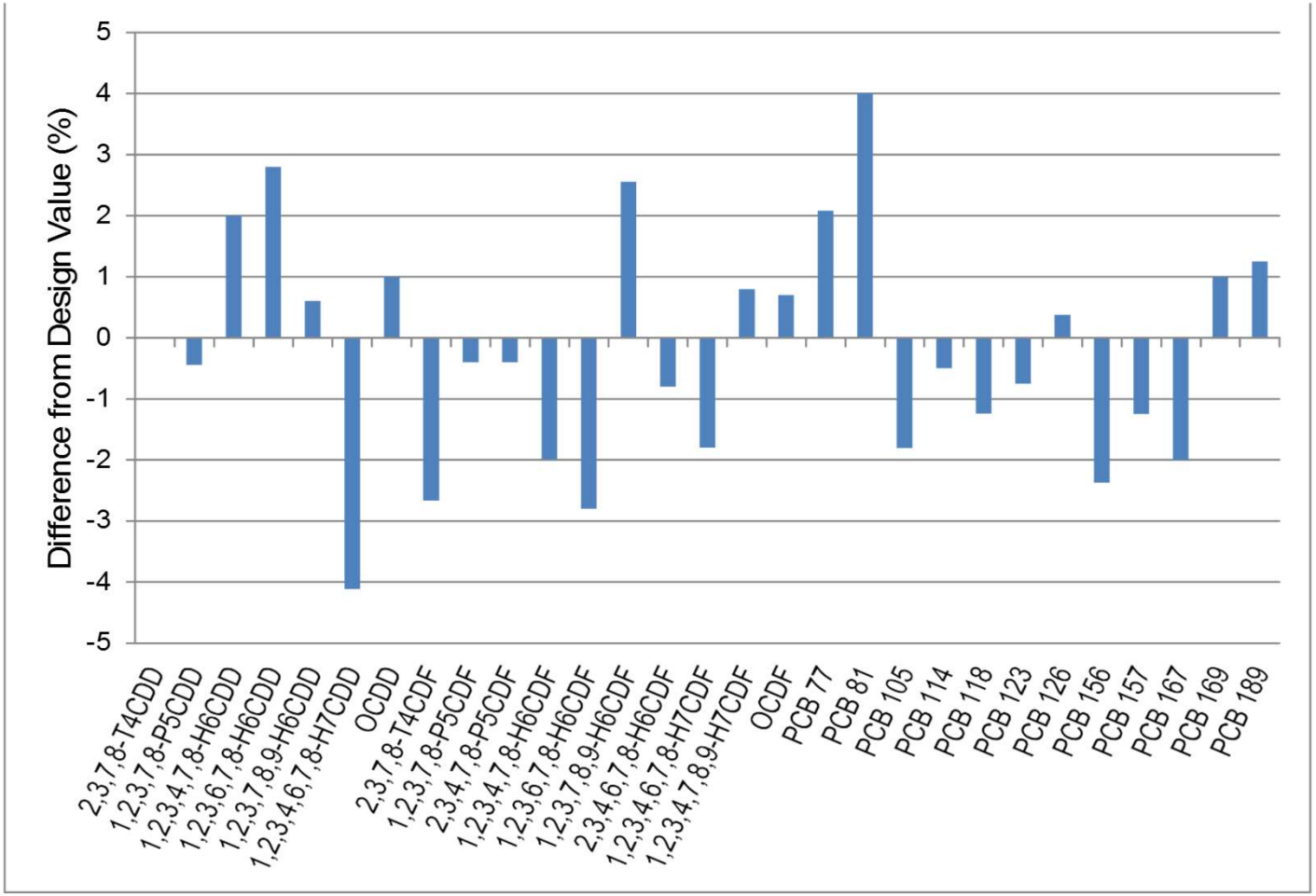
Results in ng/g

Ontario

Northern Contaminants Program (NCP)

- The NCP is a Performance Evaluation (PE) program used to monitor the accuracy and precision of testing laboratories.
- MOECC has administered the program since 2003. Participation has grown from 19 labs in Phase 1 to 55 labs in Phase 10. Phase 10 samples currently in labs for analysis.
- Each Phase includes 1 inject ready analytical standard, 3 or 4 CRMs/SRMs and 1 or 2 uncertified reference materials
- Analytical tests include Dioxins, PCBs, PBDEs and HFR, PFAAs, OC Pesticides, PCNs, OPFRs, metals, organometalics

Phase 9 – Injection ready Standard Dioxins / DLPCBs



Isotope Dilution with High Resolution Mass Spectrometry N = 8 to 11

Ontario

Fish CRM Dioxin comparison

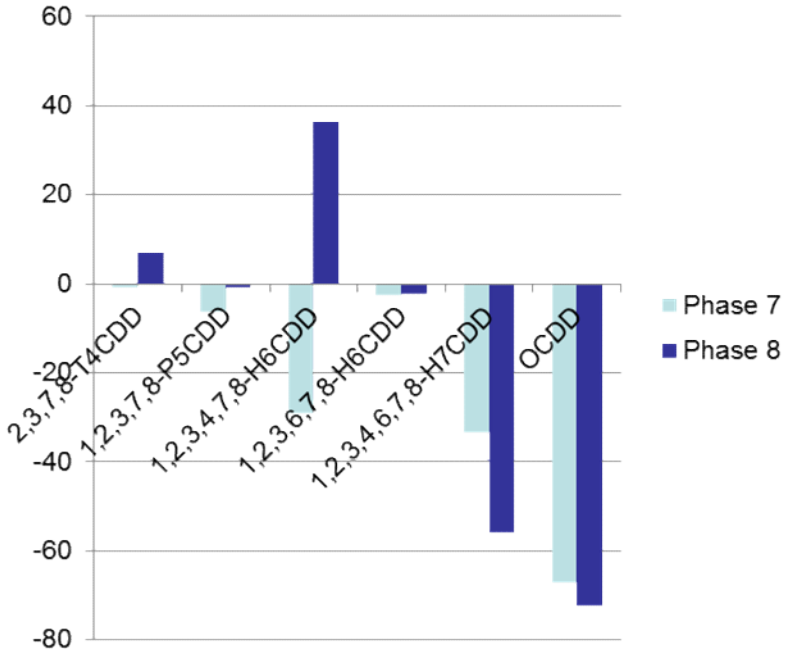
Analyte	WMF-01				EDF-2526				NRC Carp-2			
	Design	Median	Robust Std. Dev.	N	Design	Median	Robust Std. Dev.	N	Design	Median	Robust Std. Dev.	N
2,3,7,8-T4CDD	13.1	13.0	1.97	11	19.7	20.9	3.68	12	7.40	7.18	1.65	11
1,2,3,7,8-P5CDD	2.72	2.55	0.275	12	39.9	41.2	11.6	12	5.30	4.55	0.548	12
1,2,3,4,7,8-H6CDD	0.220	0.156	0.101	4	54.9	52.3	10.6	12	1.60	1.63	0.496	12
1,2,3,6,7,8-H6CDD	0.880	0.857	0.116	9	51.1	50.0	12.1	12	5.80	5.31	1.10	12
1,2,3,7,8,9-H6CDD	0.270	0.235	0.288	6	52.9	54.0	13.4	12	0.780	0.718	0.155	11
1,2,3,4,6,7,8-H7CDD	0.590	0.393	0.251	8	70.7	72.9	17.4	12	6.40	6.32	2.53	12
OCDD	3.91	1.28	0.630	8	181	179	37.3	12	9.40	7.93	1.75	11
2,3,7,8-T4CDF	13.1	12.4	1.52	12	18.7	19.9	4.80	12	18.2	17.1	4.95	12
1,2,3,7,8-P5CDF	1.53	1.17	0.245	12	39.0	41.4	7.35	12	5.60	6.34	1.71	12
2,3,4,7,8-P5CDF	7.15	6.27	1.13	12	37.8	38.0	7.58	12	-	14.4	2.70	12
1,2,3,4,7,8-H6CDF	0.860	0.757	0.449	8	83.3	82.7	12.5	12	-	4.05	0.980	12
1,2,3,6,7,8-H6CDF	0.510	0.576	0.326	7	62.8	62.0	14.9	12	-	2.62	0.670	12
1,2,3,7,8,9-H6CDF	0.250	0.376	0.327	4	57.3	58.4	12.5	12	-	0.113	0.101	4
2,3,4,6,7,8-H6CDF	0.680	0.531	0.218	8	58.6	59.8	8.60	12	-	1.49	0.233	12
1,2,3,4,6,7,8-H7CDF	1.01	0.554	0.470	7	81.6	81.8	19.9	12	-	4.39	0.933	11
1,2,3,4,7,8,9-H7CDF	0.300	0.268	0.302	5	76.7	78.6	19.6	12	-	0.268	0.140	4
OCDF	1.38	0.750	0.300	7	185	172	30.8	12	-	0.768	0.340	8

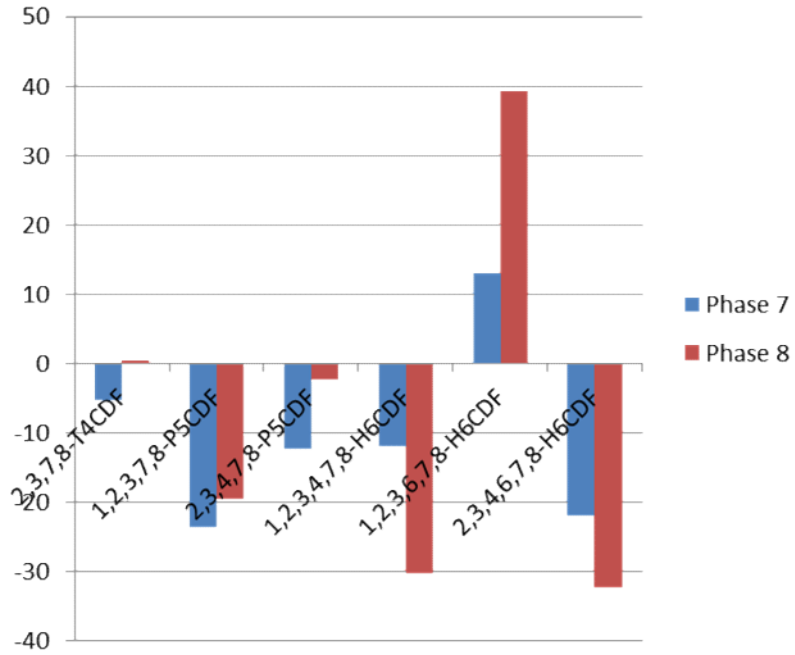
Results in pg/g

Ontario

Fish CRM Dioxin comparison

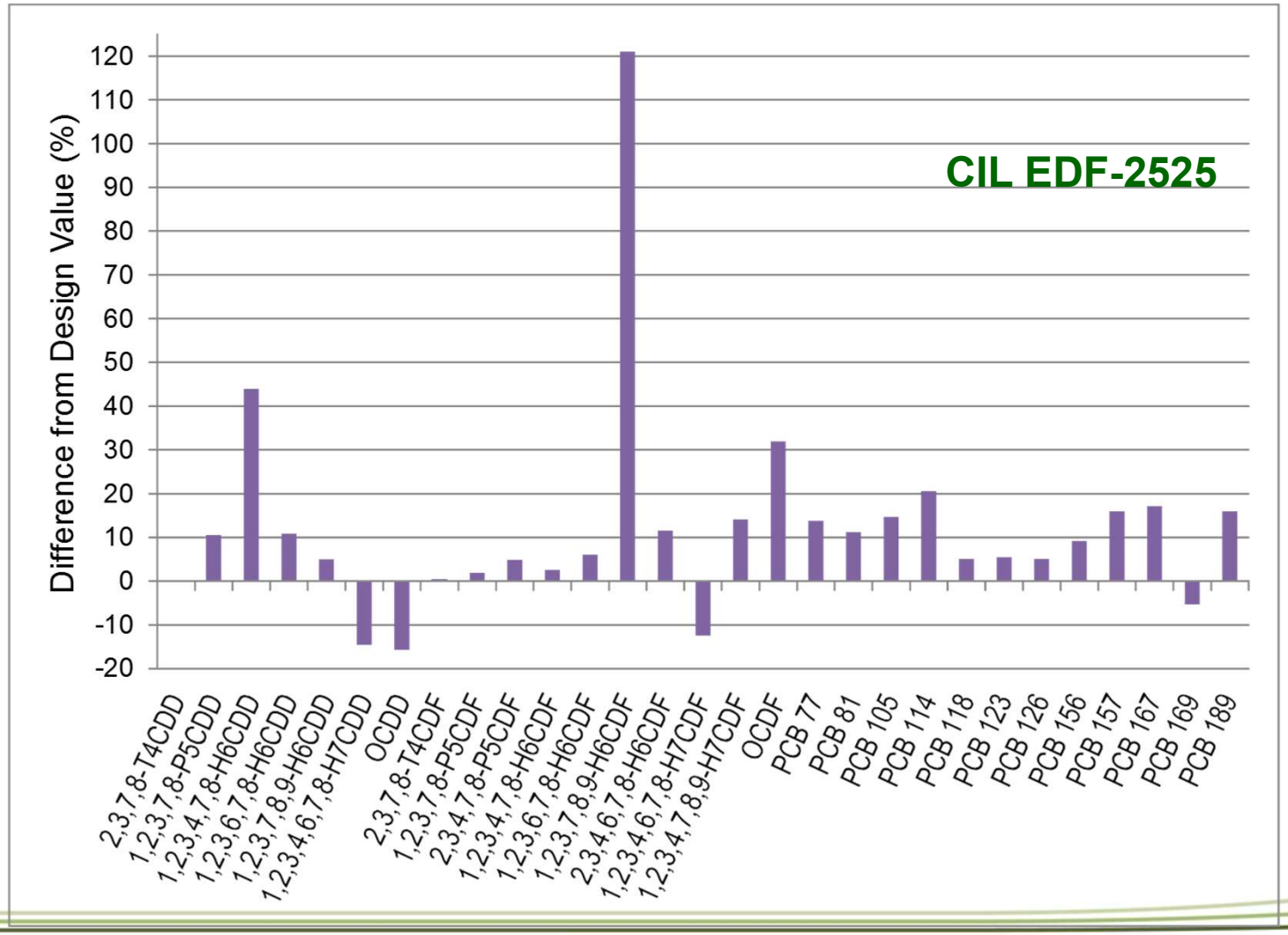
WMF-01





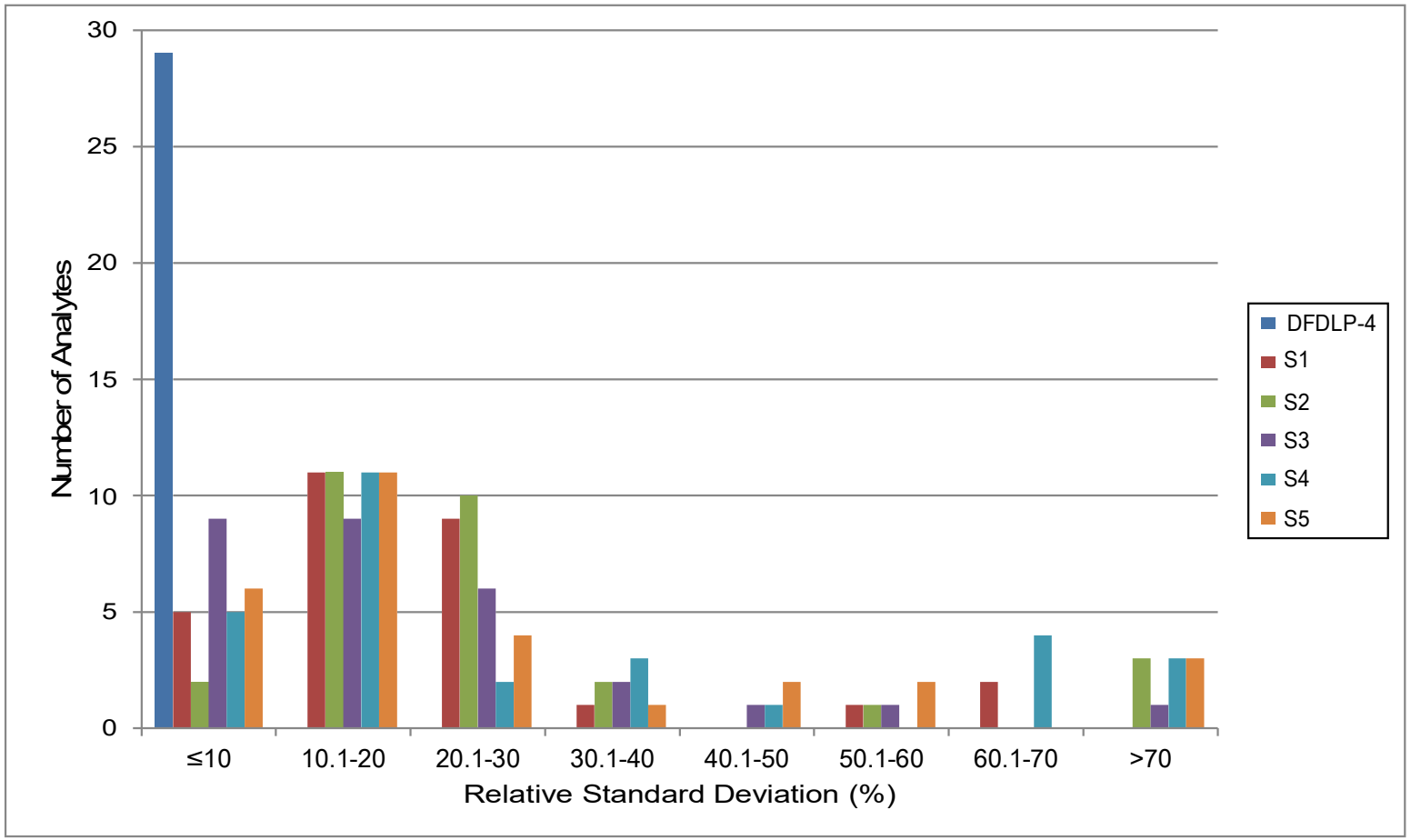
Ontario

Fish CRM Dioxin comparison



Ontario

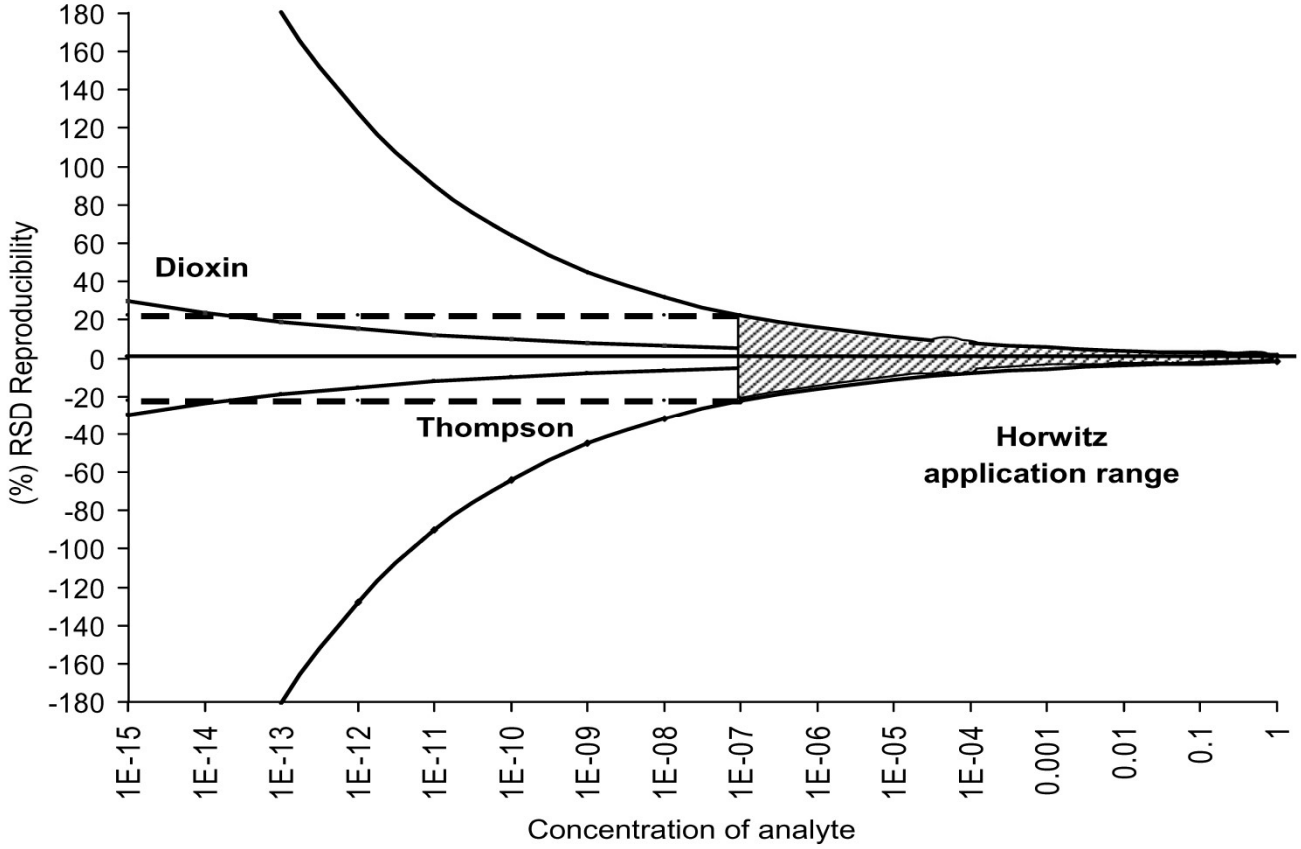
Phase 9 - Relative Standard Deviation - Dioxins / DLPCBs



DFDLP - 4 = IRS, S1 =NRC Carp, S2 = WMF-01, S3 = EDF-2525, S4 = NIST 2976, S5 = Lake Superior Lake Trout extract

Ontario

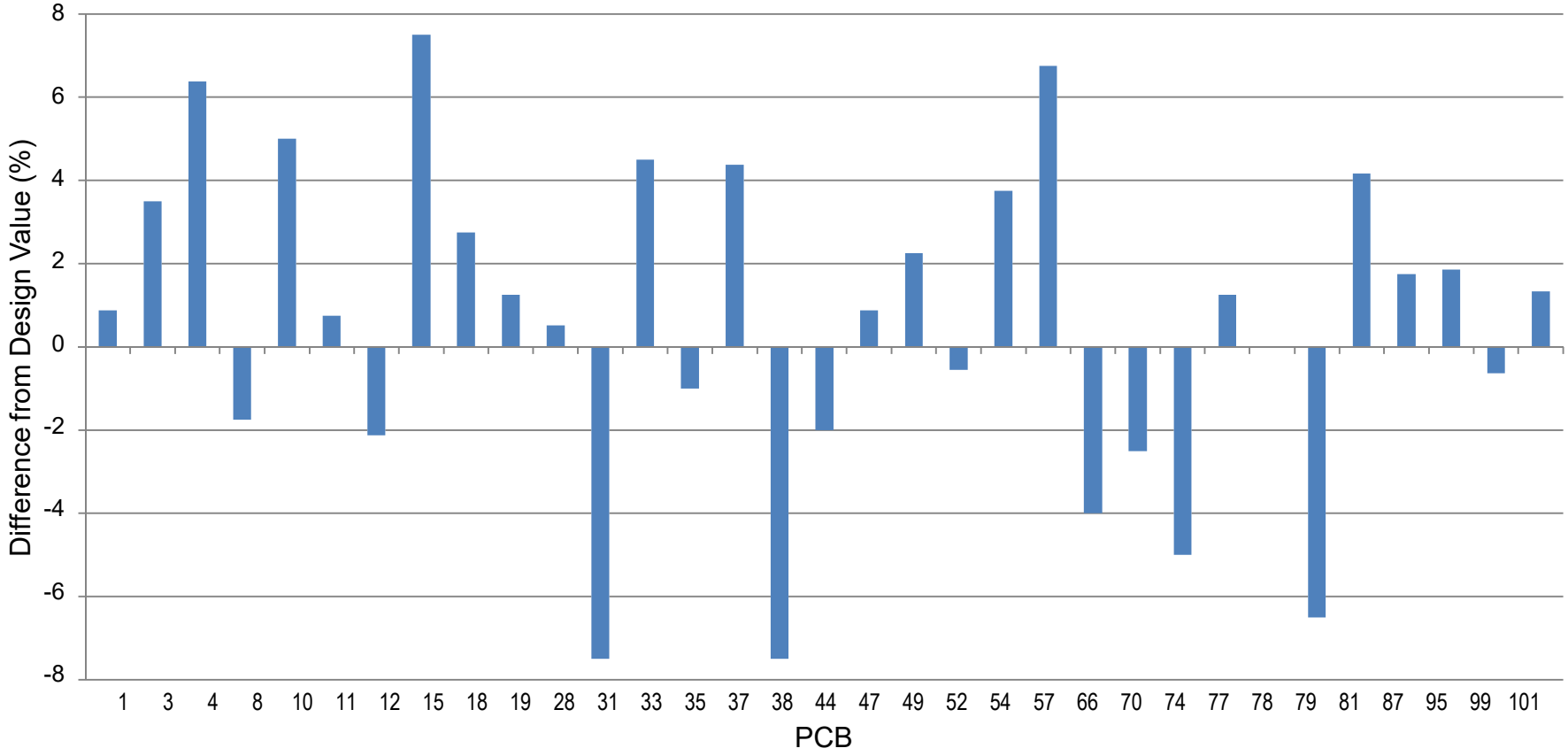
Dioxin Analyical Uncertainty



Horowitz et al, JAOAC 63, 1344 (1980)

Ontario

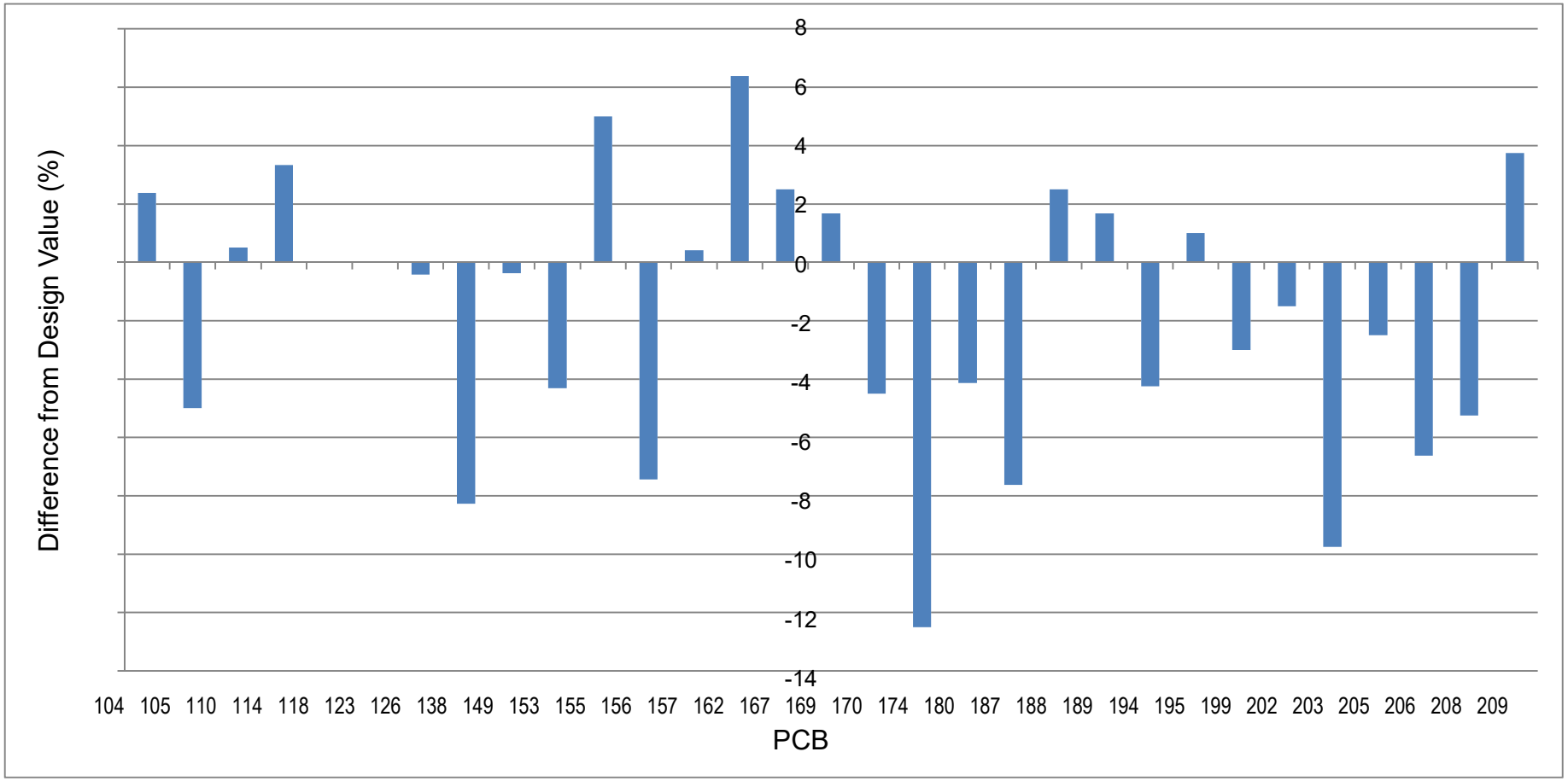
Phase 9 – Injection ready Standard Congener PCBs



Internal Standard Gas Chromatography Mass Spectrometry N = 3 to 20

Ontario

Phase 9 – Injection ready Standard Congener PCBs

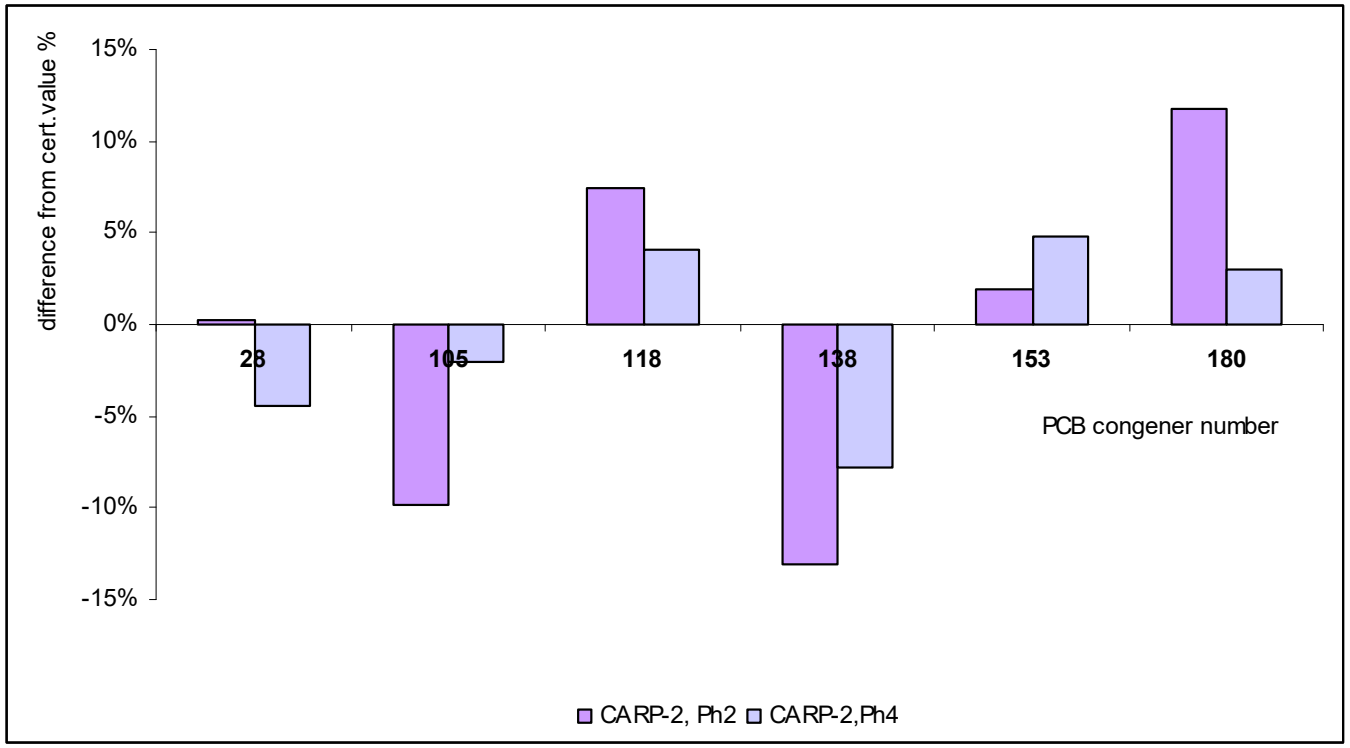


Internal Standard Gas Chromatography Mass Spectrometry N = 3 to 20

Ontario

Fish CRM comparison

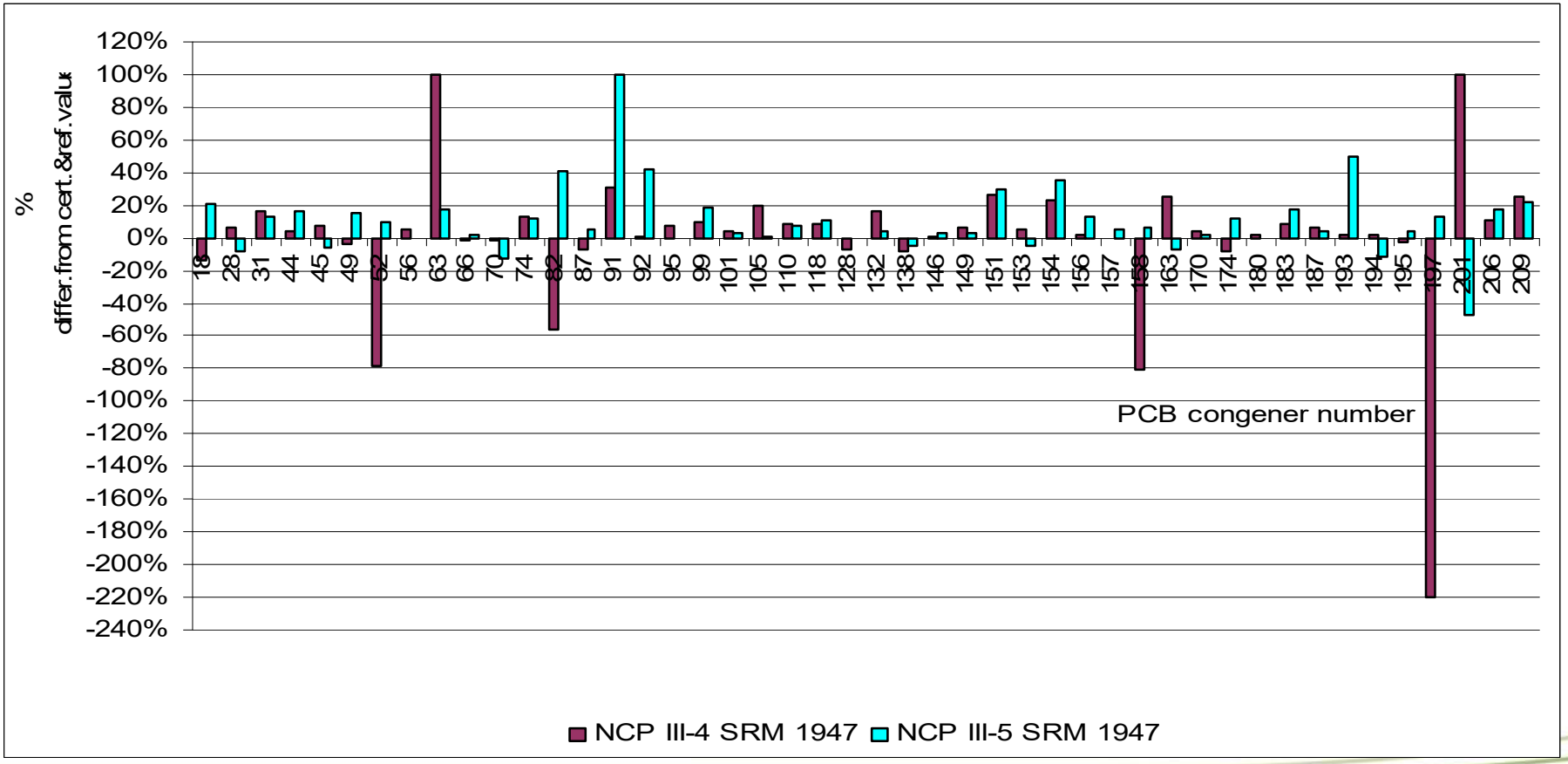
NRC Carp - 2



Ontario

Fish CRM comparison

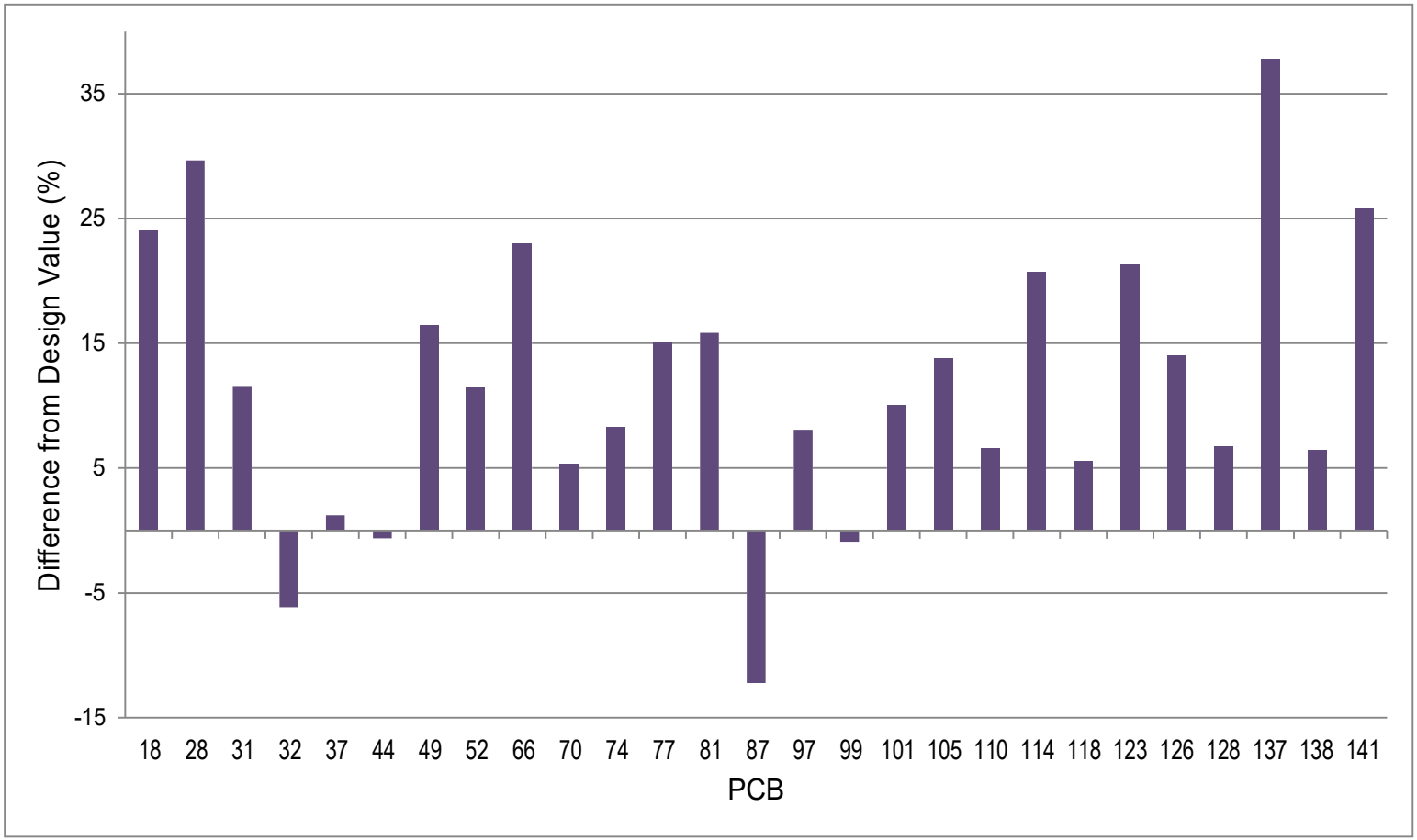
NIST SRM 1947



N=8

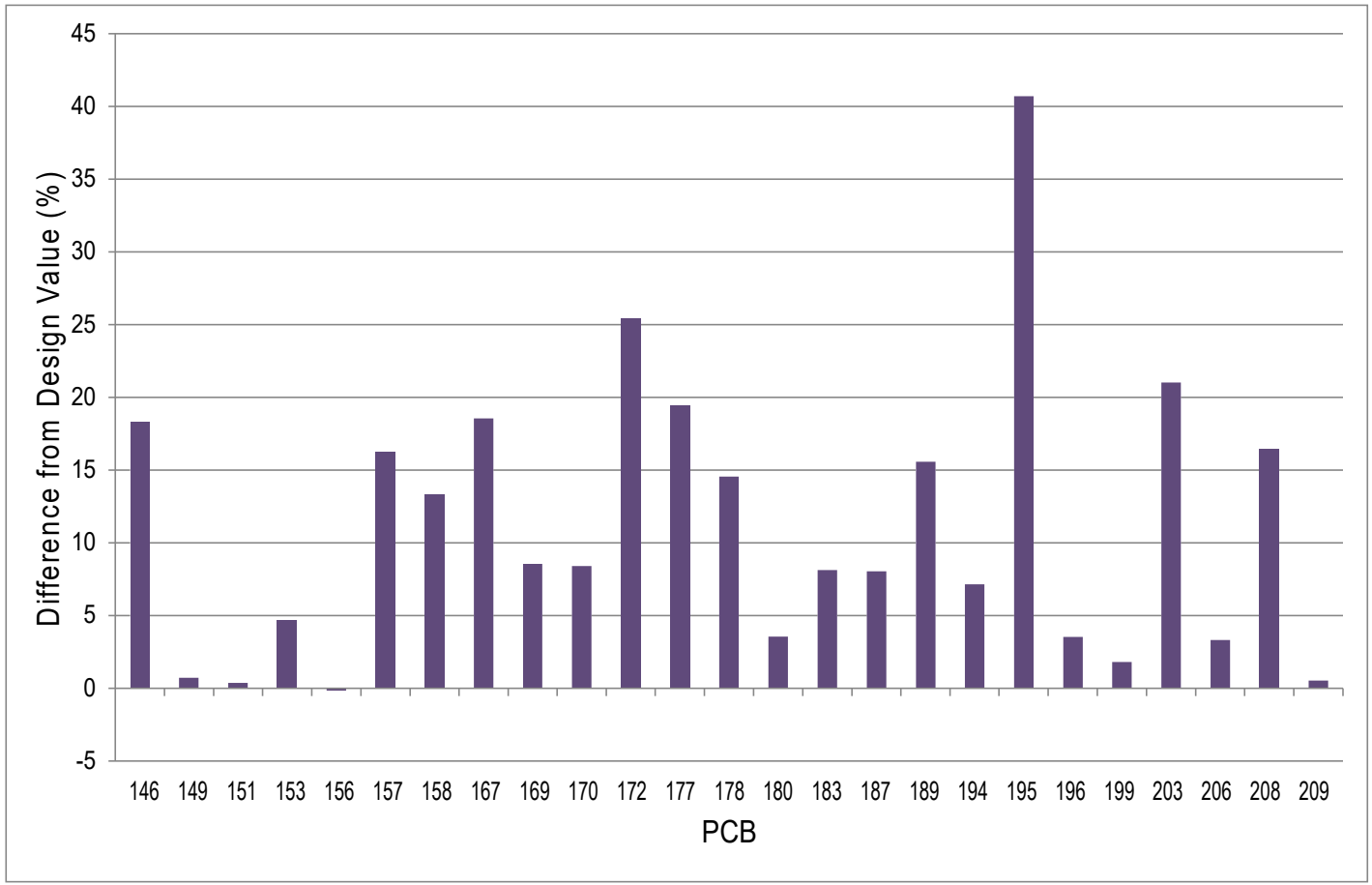
Ontario

Phase 9 EDF – 2525 Congener PCBs



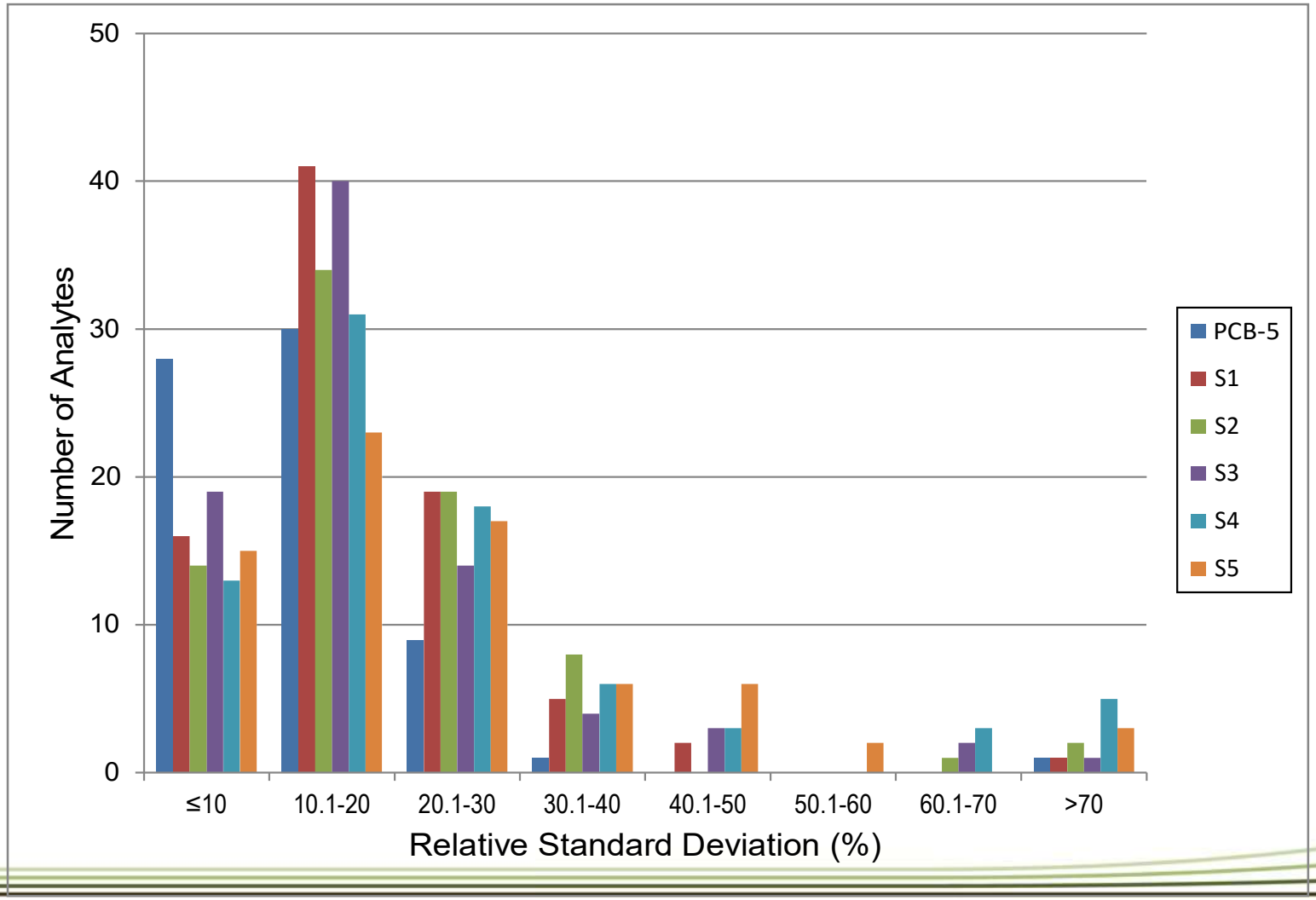
Ontario

Phase 9 EDF – 2525 Congener PCBs



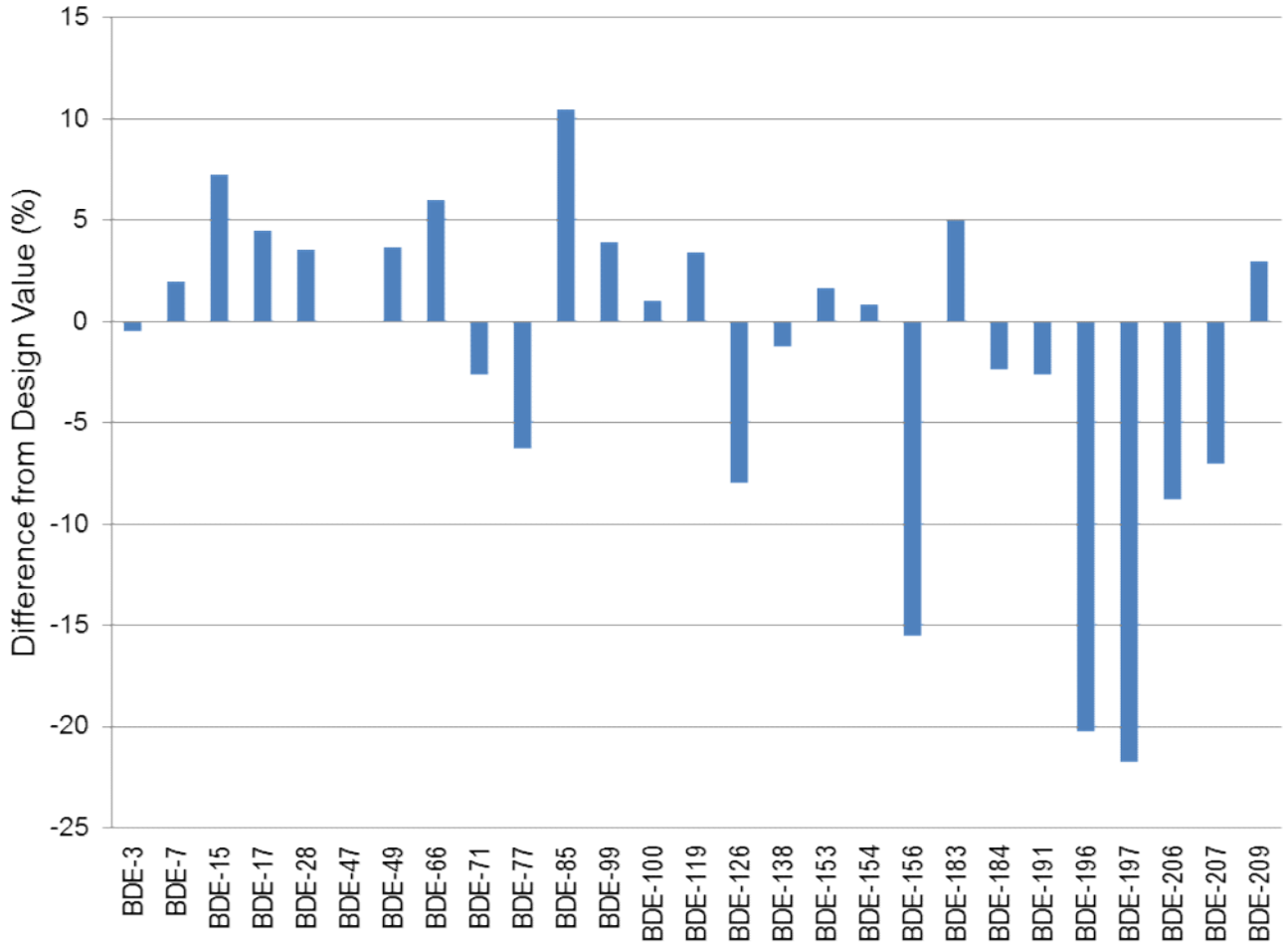
Ontario

Phase 9 - Relative Standard Deviation PCBs



Ontario

Phase 9 – Injection ready Standard PBDEs



Ontario

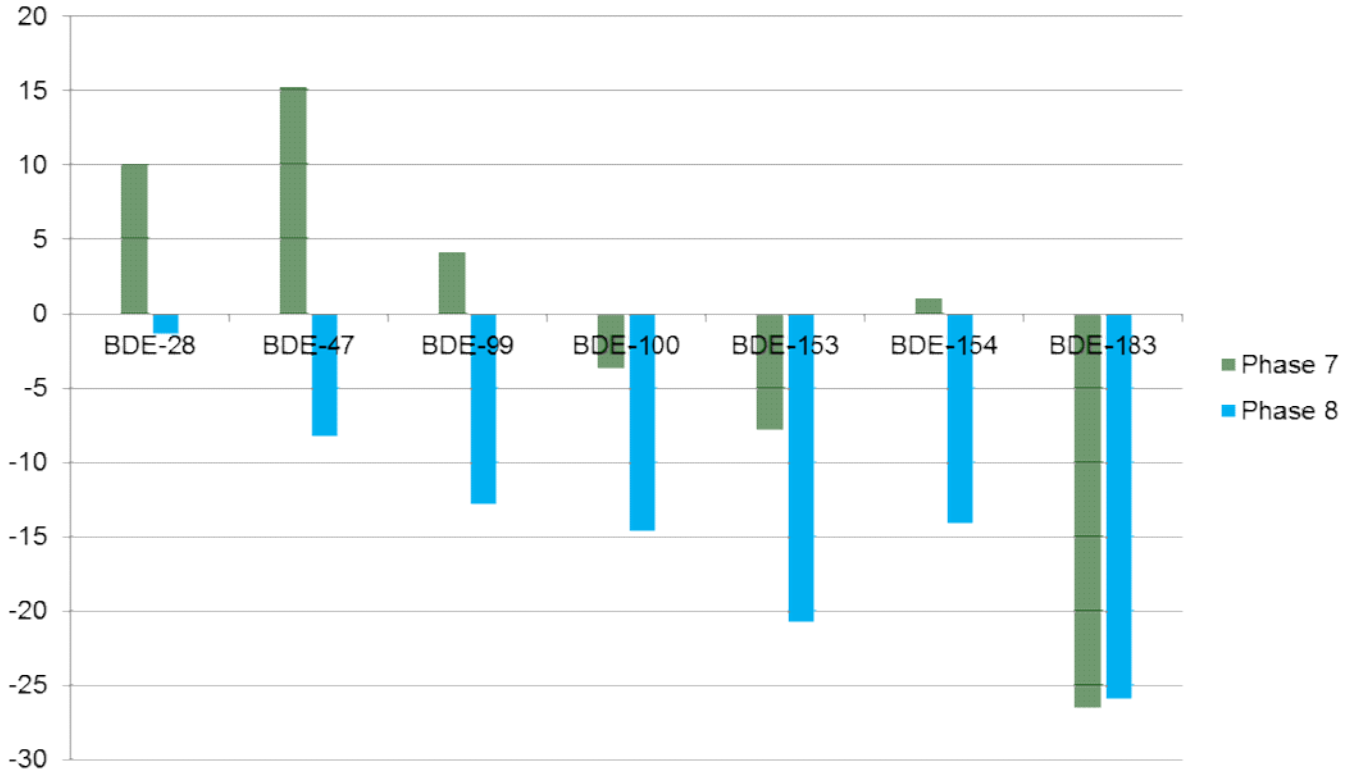
Fish CRM PBDE comparison

Analyte	WMF-01 Phase 7				WMF-01 Phase 8				EDF 252 6 Phase 8			
	Design	*Median*	*Robust SD*	*N*	*Design*	*Median*	*Robust SD*	*N*	*Design*	*Median*	*Robust SD*	*N*
BDE-28	3.12	3.44	0.39	14	3.12	3.08	1.29	16	-	7.96	9.86	7
BDE-47	123	142	28.4	18	123	113	52.5	19	-	42.0	63.0	11
BDE-99	37.5	39.1	9.52	18	37.5	32.7	13.5	20	-	19.2	26.3	10
BDE-100	35.9	34.6	7.28	18	35.9	30.6	12.5	20	-	10.5	10.1	7
BDE-119	-	1.21	0.96	5	-	0.636	0.373	6	-			0
BDE-153	17.0	15.7	3.65	18	17.0	13.5	3.40	20	7.48	3.56	4.13	4
BDE-154	19.8	20.0	2.33	16	19.8	17.0	5.40	17	-	2.45	2.07	3
BB-153	-			2	-	3.10	0.450	3	-			0
BDE-183	0.532	0.391	0.071	12	0.532	0.394	0.125	16	-	-	-	2
BDE-209	n/a	0.100	0.035	4	-	0.227	0.167	8	-	2.59	3.13	3

Results in ng/g

Ontario

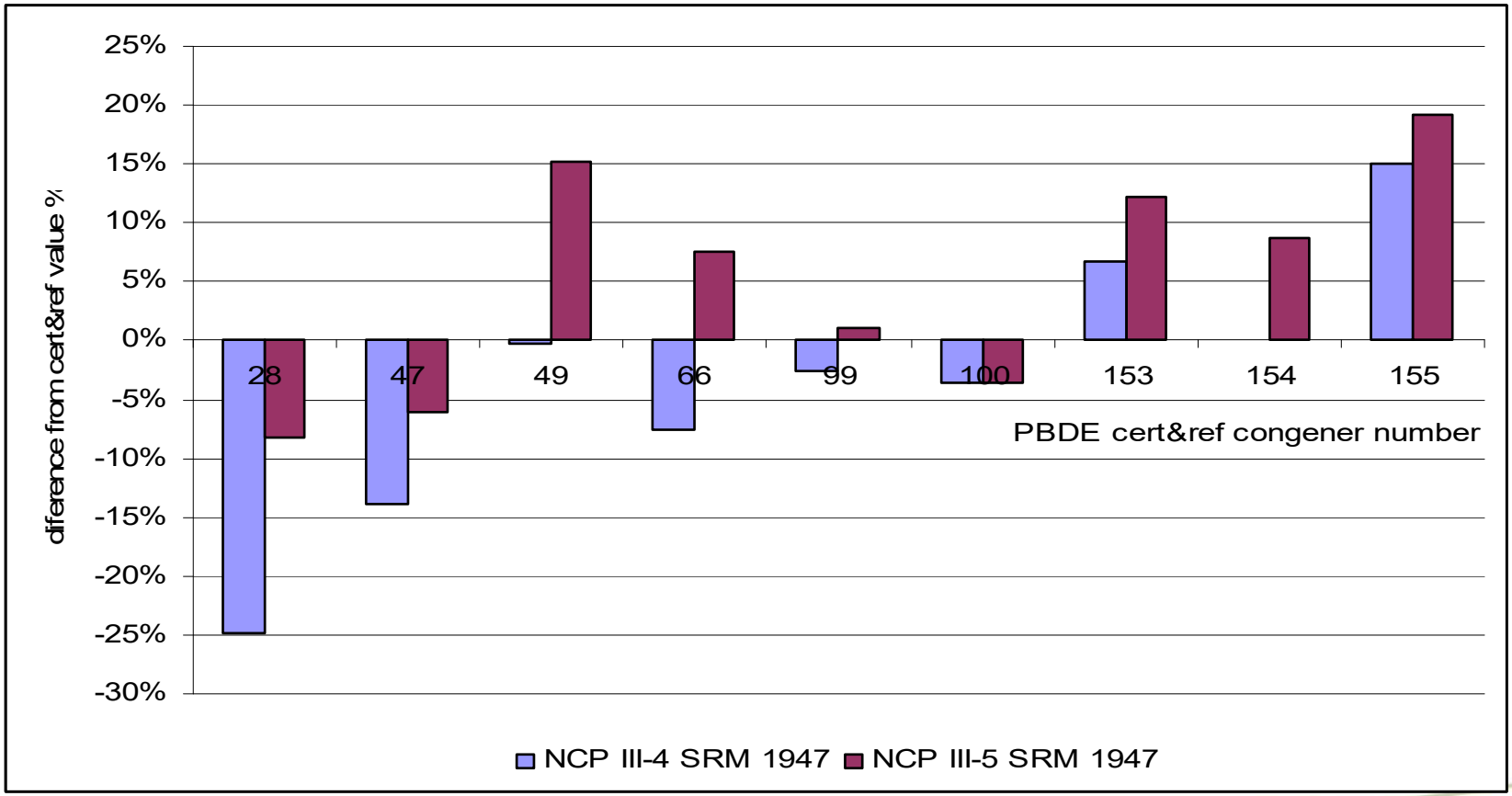
WMF-01 Fish CRM PBDE comparison



Ontario

Fish CRM comparison

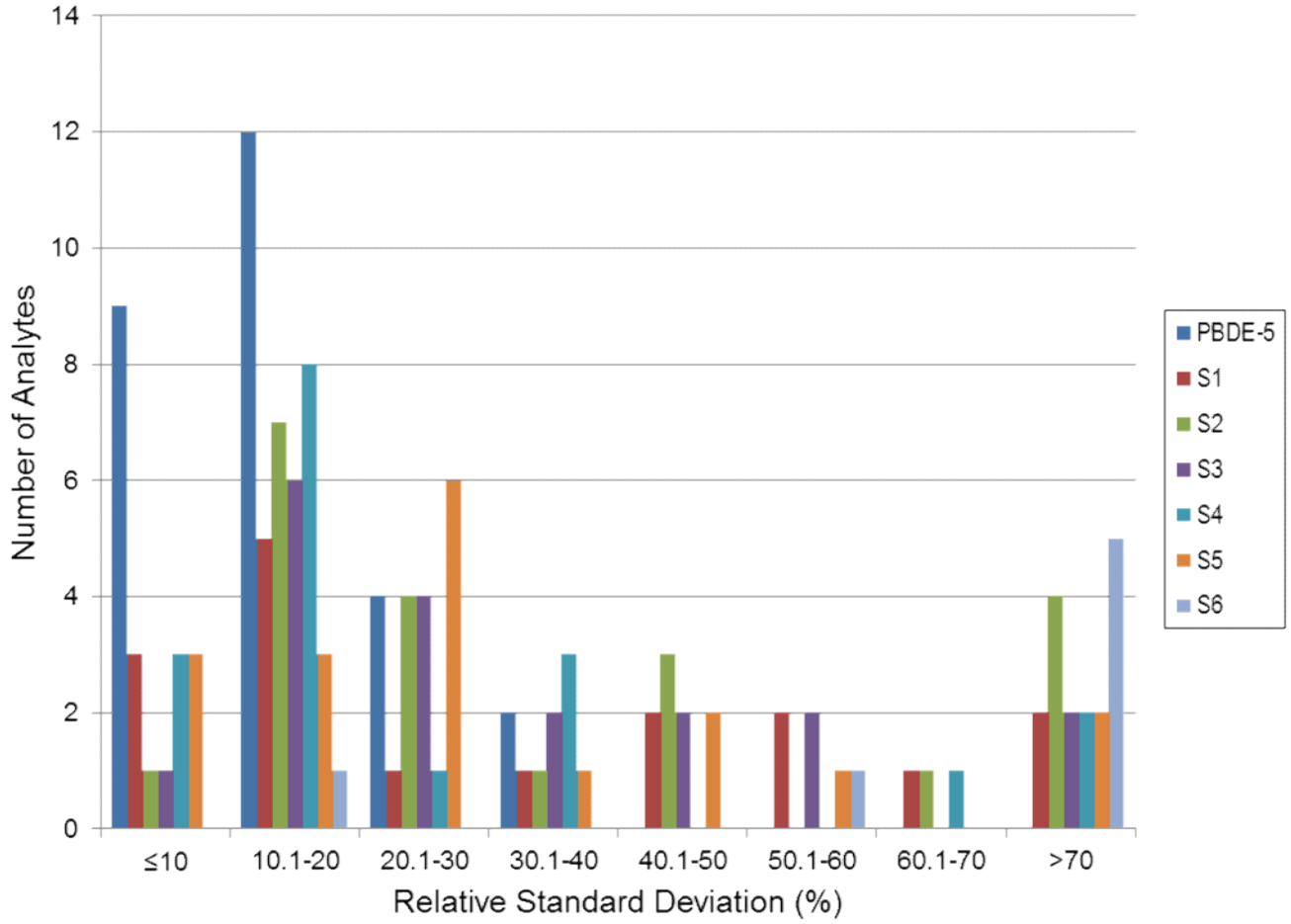
NIST SRM 1947



N=8

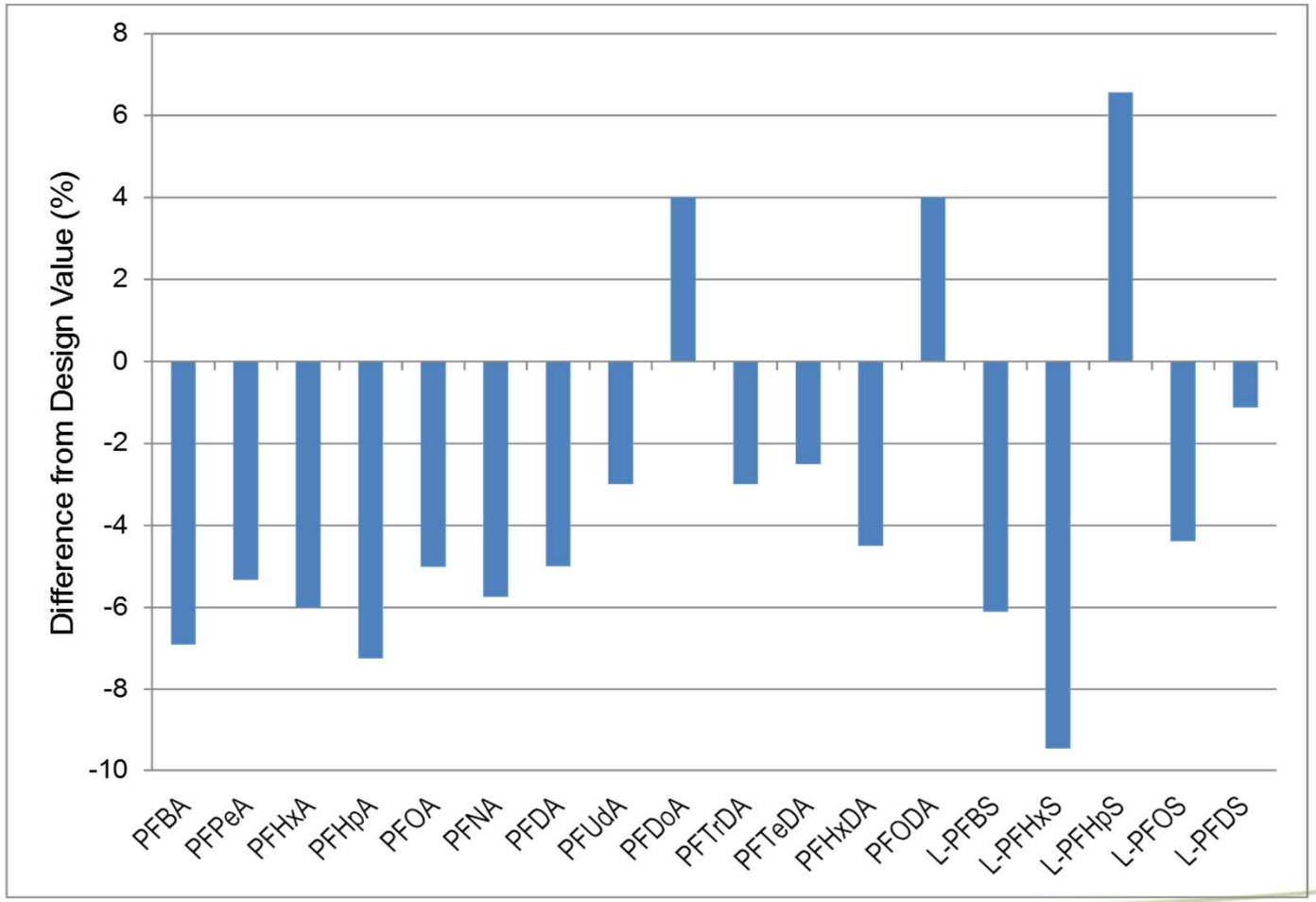
Ontario

Phase 9 - Relative Standard Deviation PBDEs



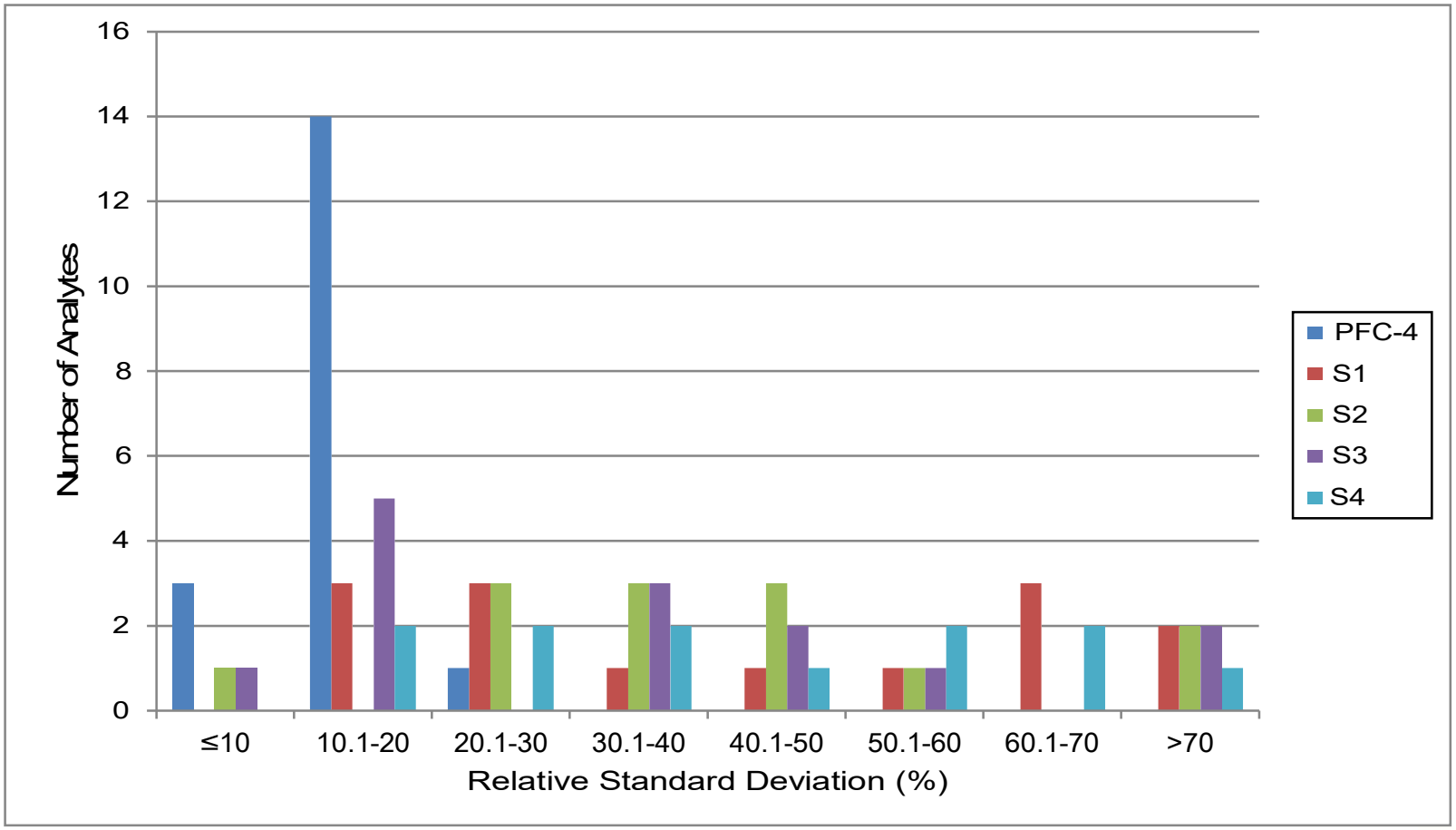
Ontario

Phase 9 Injection Ready Standards - PFAAs



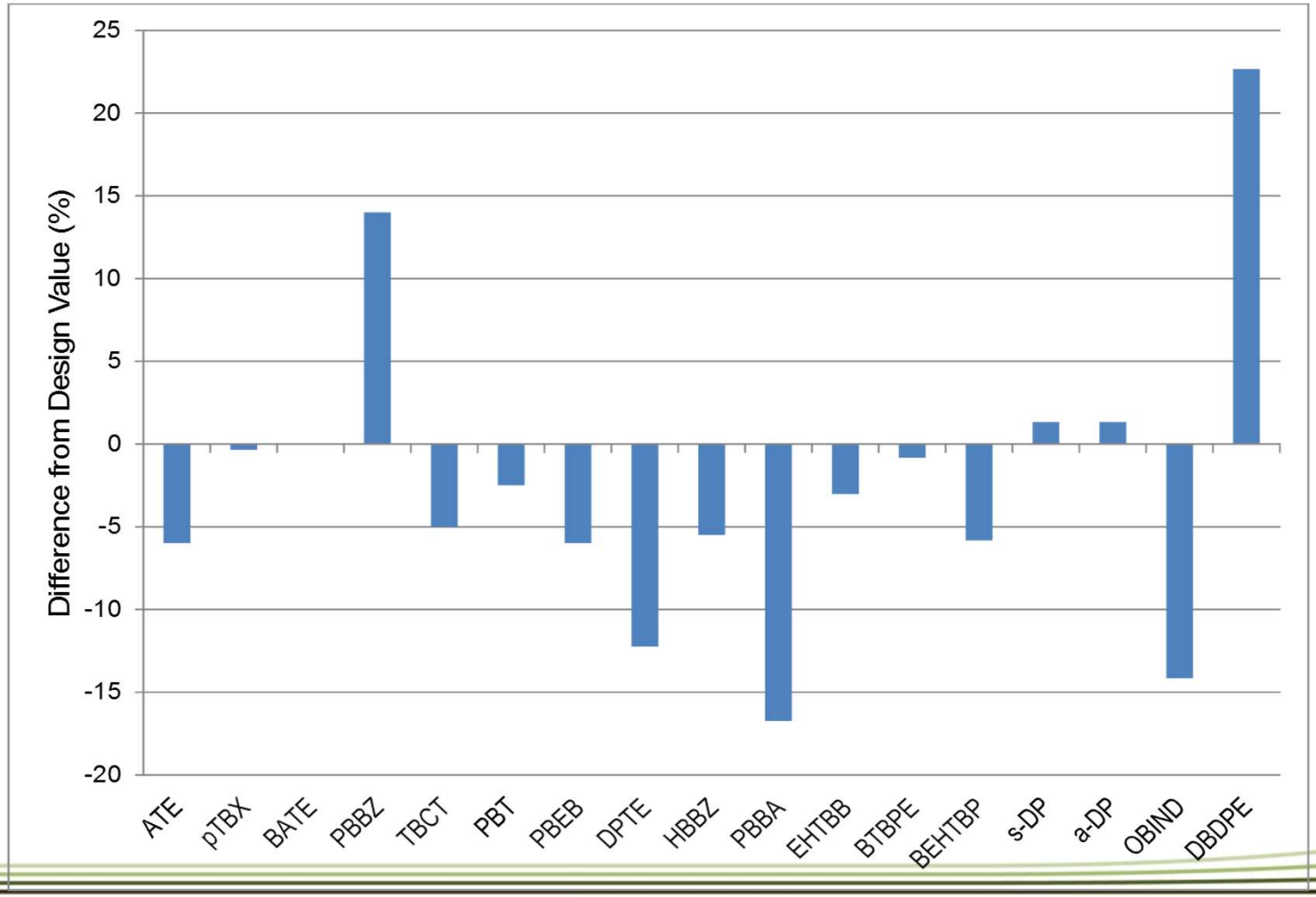
Ontario

Phase 9 - Relative Standard Deviation - PFAAs



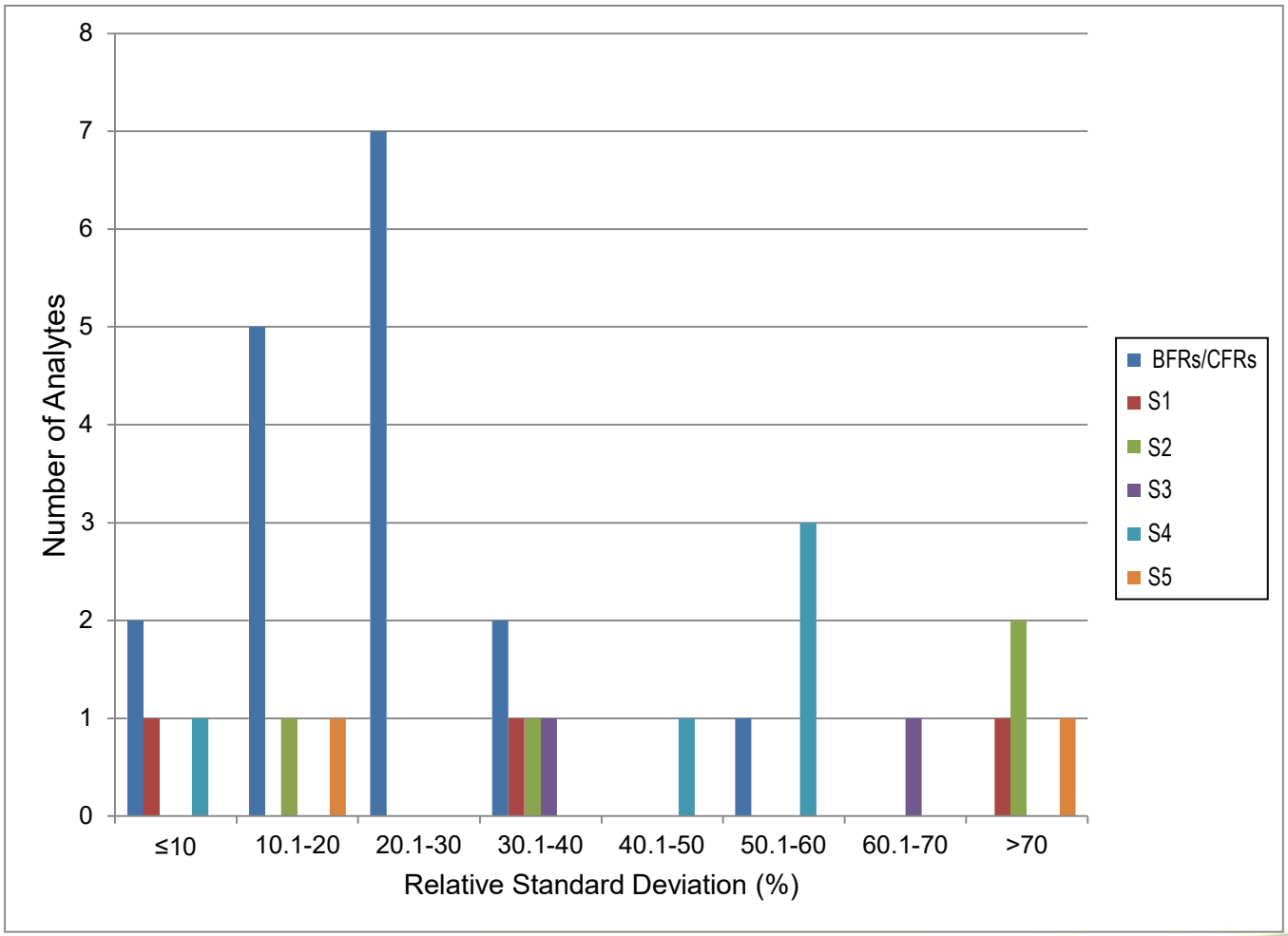
Ontario

Phase 9 – Injection ready Standard – Alternate Flame Retardants



Ontario

Phase 9 - Relative Standard Deviation – Alternate Flame Retardants

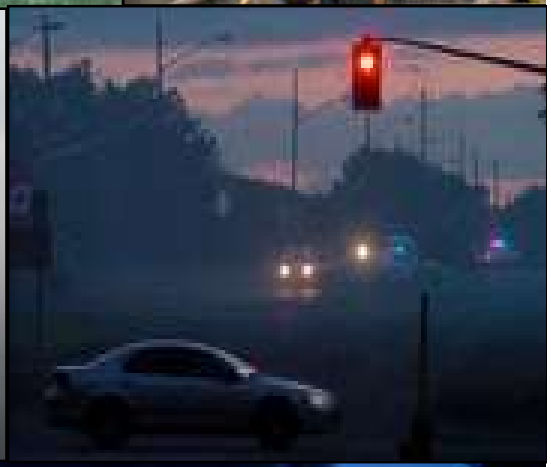


Ontario

Plastimet Recycling Plant Fire – 1997



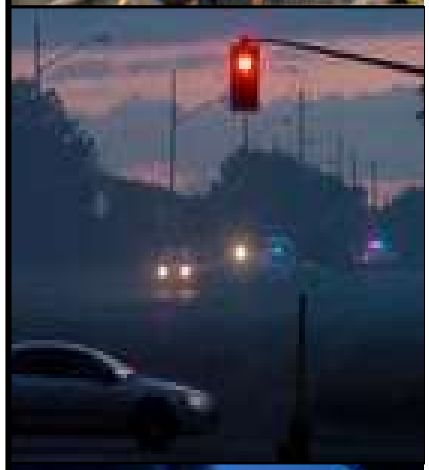



56







Plastimet

- 400+ tonnes of polyvinylchloride stored on site burned.
- The fire burned for 3 days before it was finally extinguished.
- Nearby residents were very concerned about their health.
- Several firefighters developed serious health problems.
- Chrome plating on some fire engines came off in the months following the fire due to atmospheric HCl.



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Investigation of a Lab for falsifying results

- People in surrounding the fire area were evacuated from their homes for 4 days
- Very high results for PCDD/Fs, PAH etc.
- Contracted additional samples out to a private laboratory because capacity of MOECC lab exceeded
- Contract lab reported results that were low or non-detect.
- Sent NIST 1944 to lab and indicated it was CRM NIST 1944. Reported results were within a few percent of reference values.

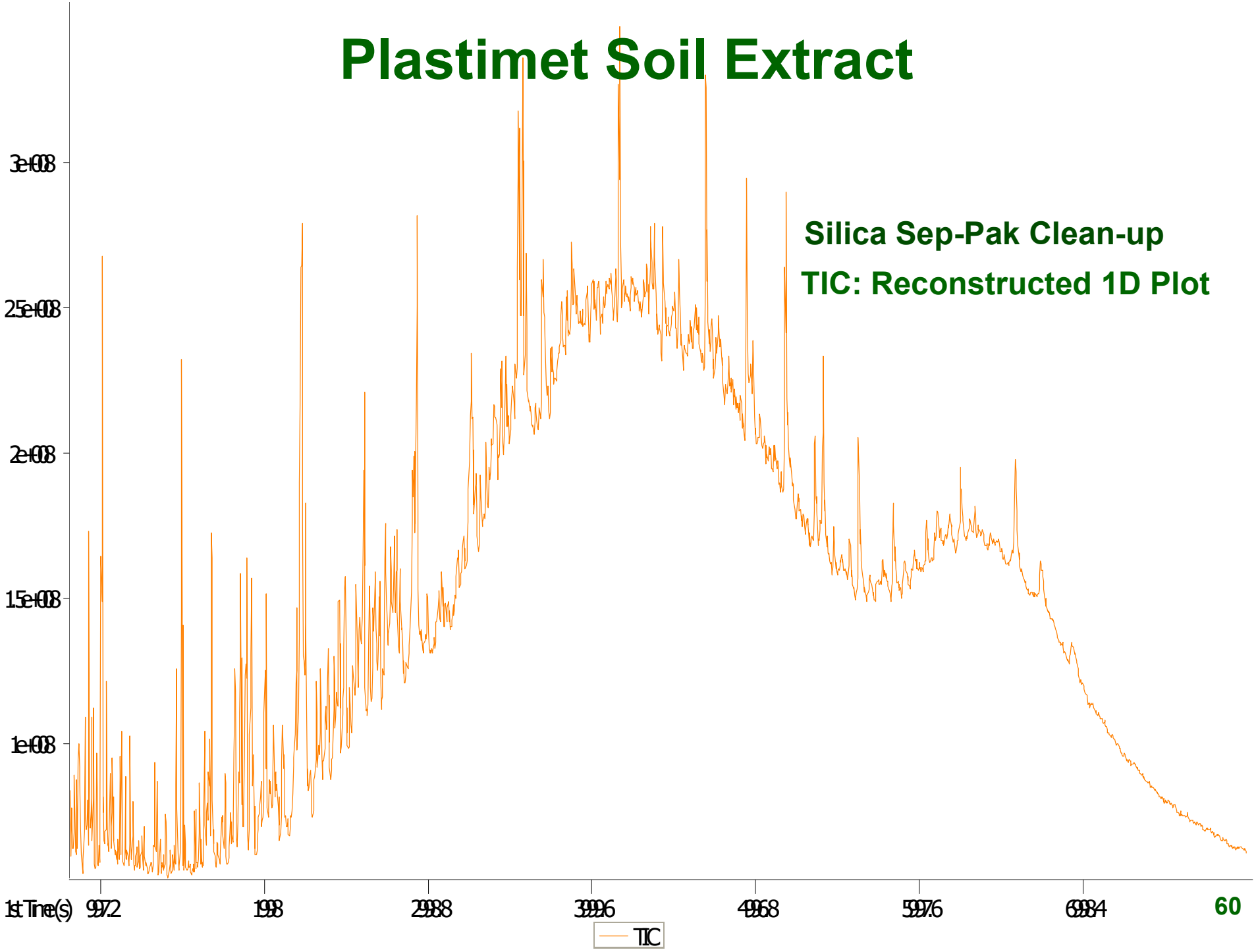
Ontario

Investigation of a Lab for falsifying results

- Resent NIST1944 and WMS-01 as blind samples to contract lab
- Results were non-detect or biased very low.
- Sent spiked water samples for PCBs and OC pesticides.
- Results were very low or non-detect.
- Resulted in the issue of a search warrant.
- Many discrepancies were observed including evidence of falsified data.
- Owners were charged and arrested.

Ontario

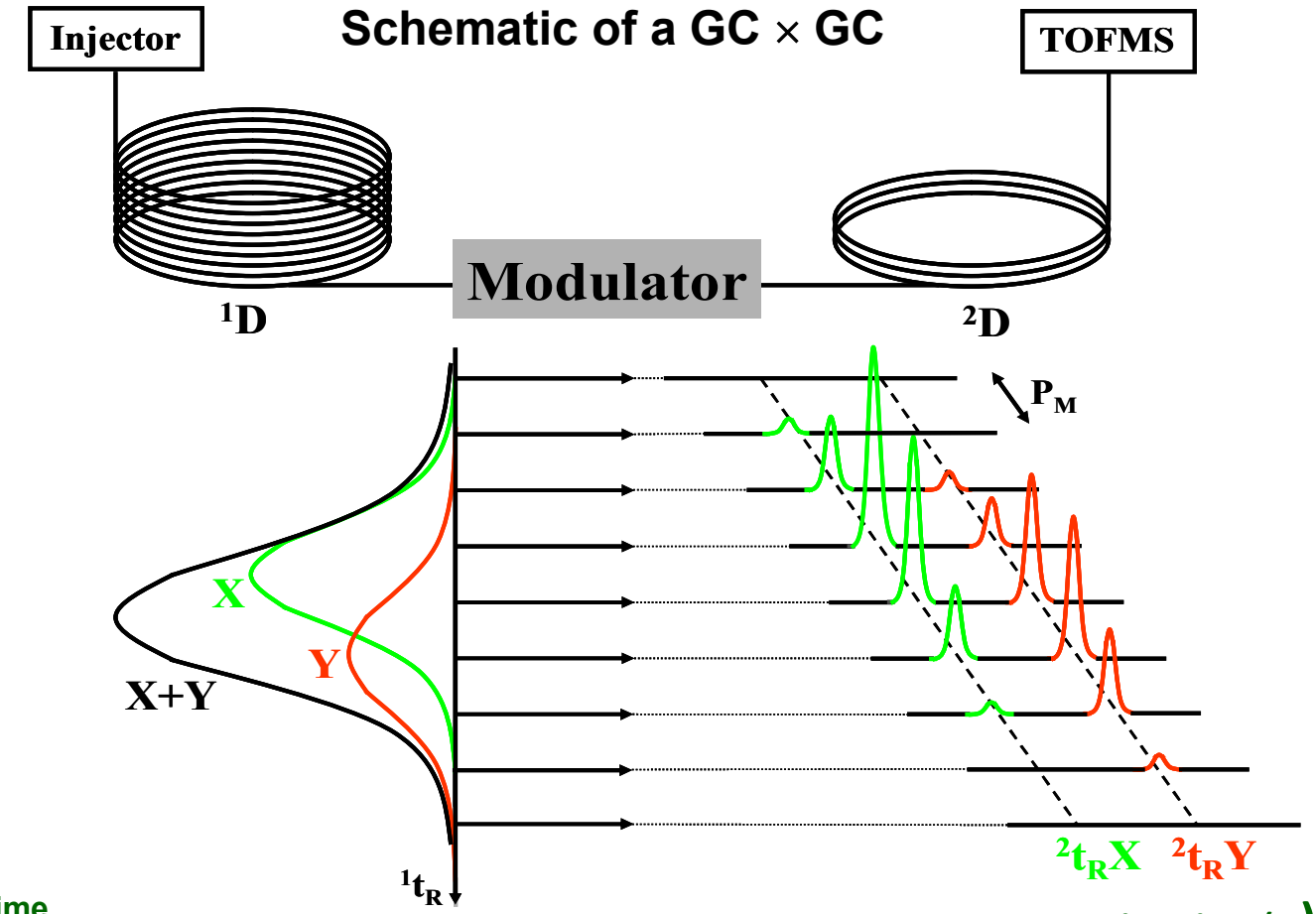
Plastimet Soil Extract



Two-Dimensional GC (GC×GC)

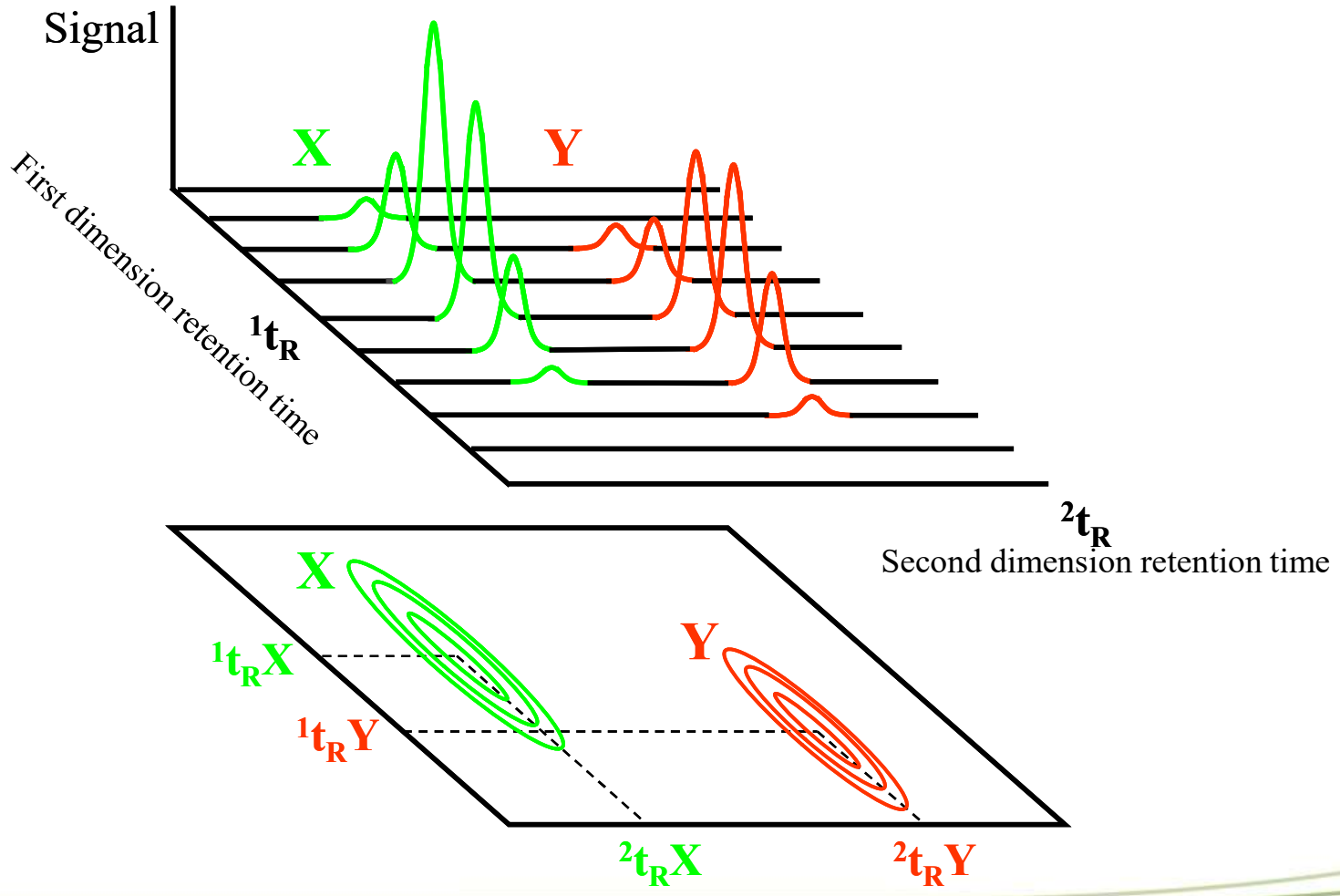
- Produces higher peak capacity (more chromatographic peaks per space). Increases peak capacity to 50 × 20 = 1000 compounds
- Eliminates the need for second column confirmation. Can do multiple analyte groups in same run and may eliminate need for extract fractionation
- Fast analysis – requires fast detector – e.g., time-of-flight mass spectrometer (TOFMS), ECD
- Provides structured chromatograms for excellent selectivity
- Provides much more information
- Results in increased sensitivity

Comprehensive two-dimensional gas chromatography



P_M = modulation time
D = dimension

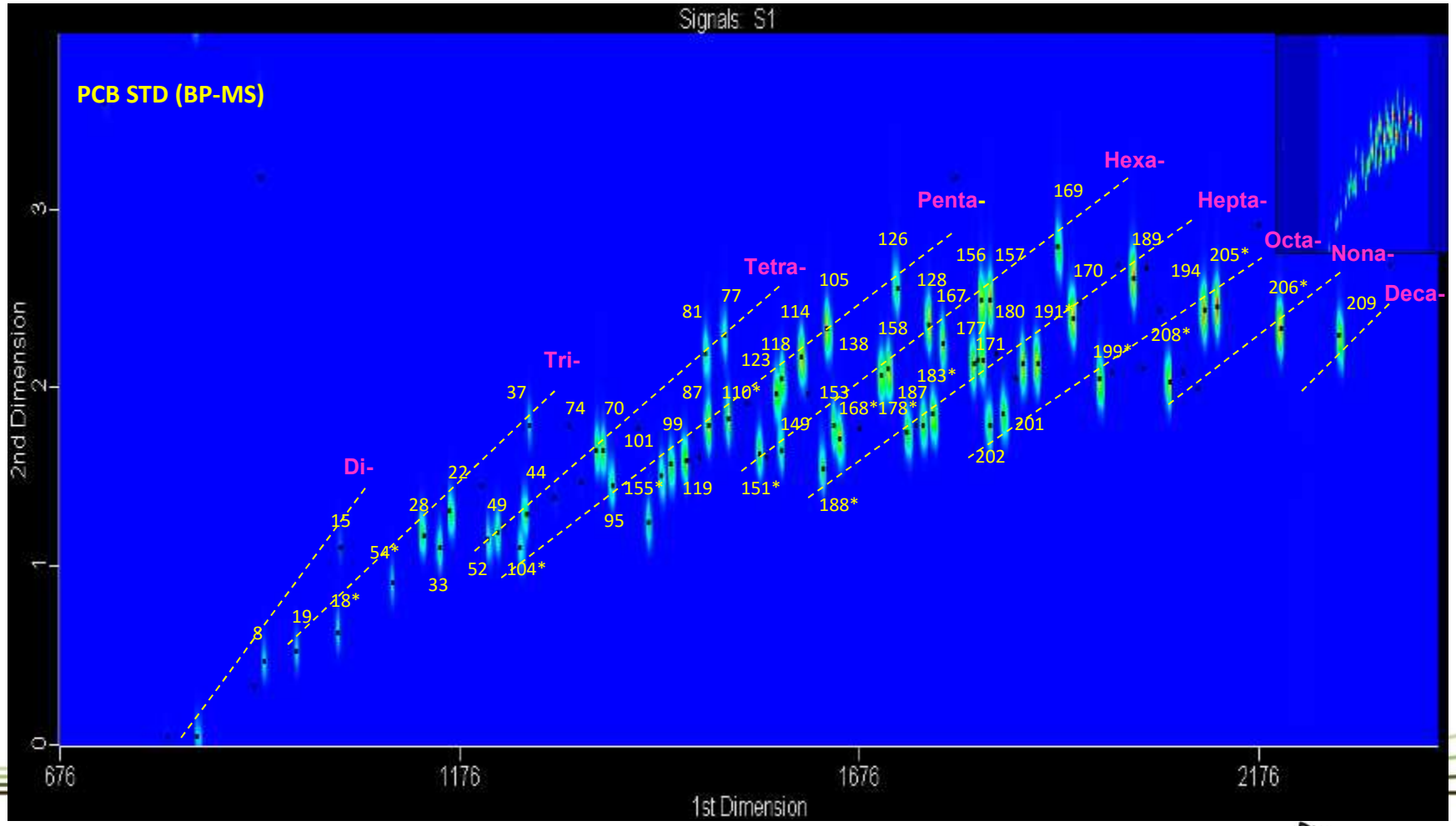
Second Dimension Modulation



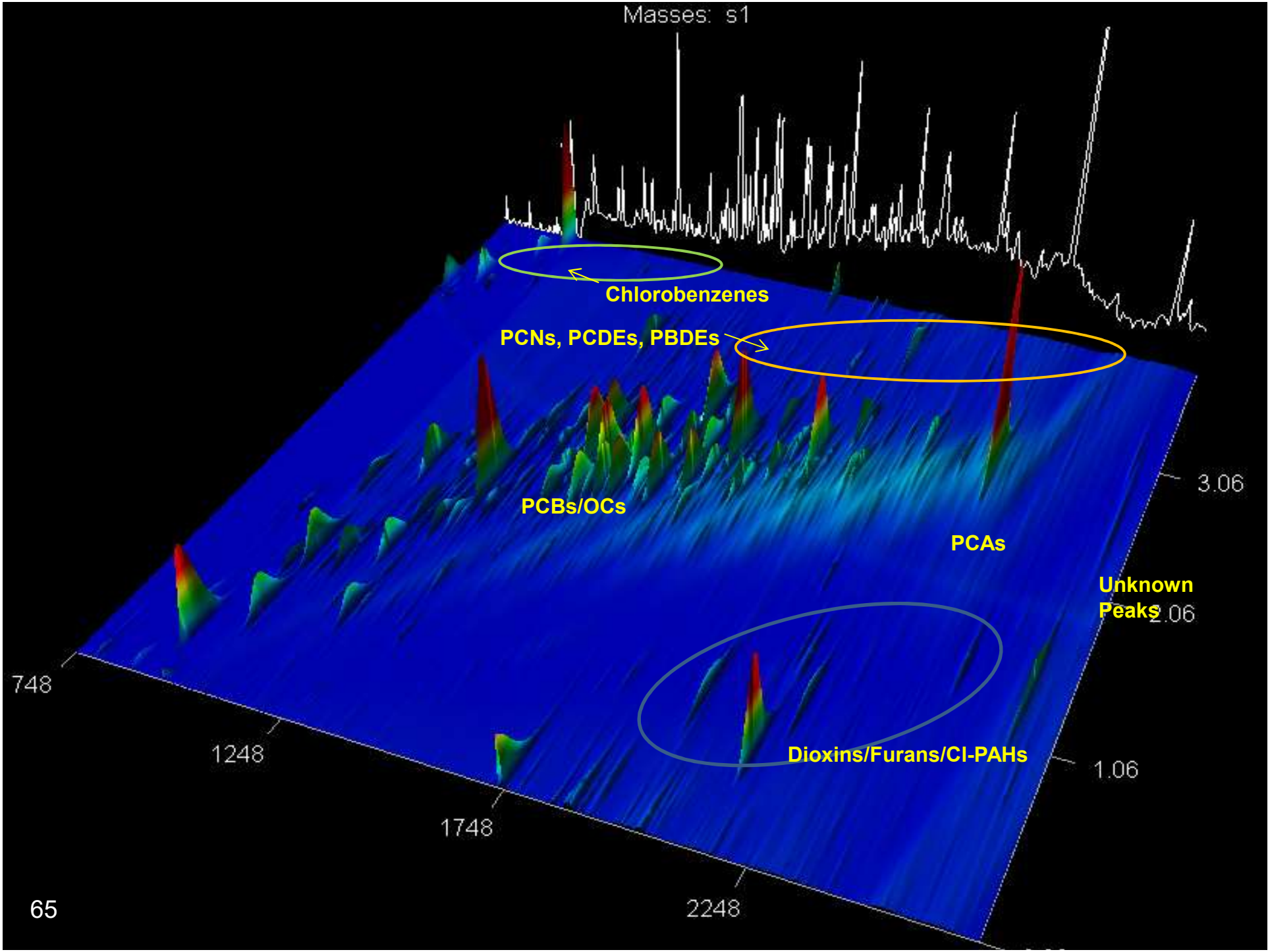
Ontario

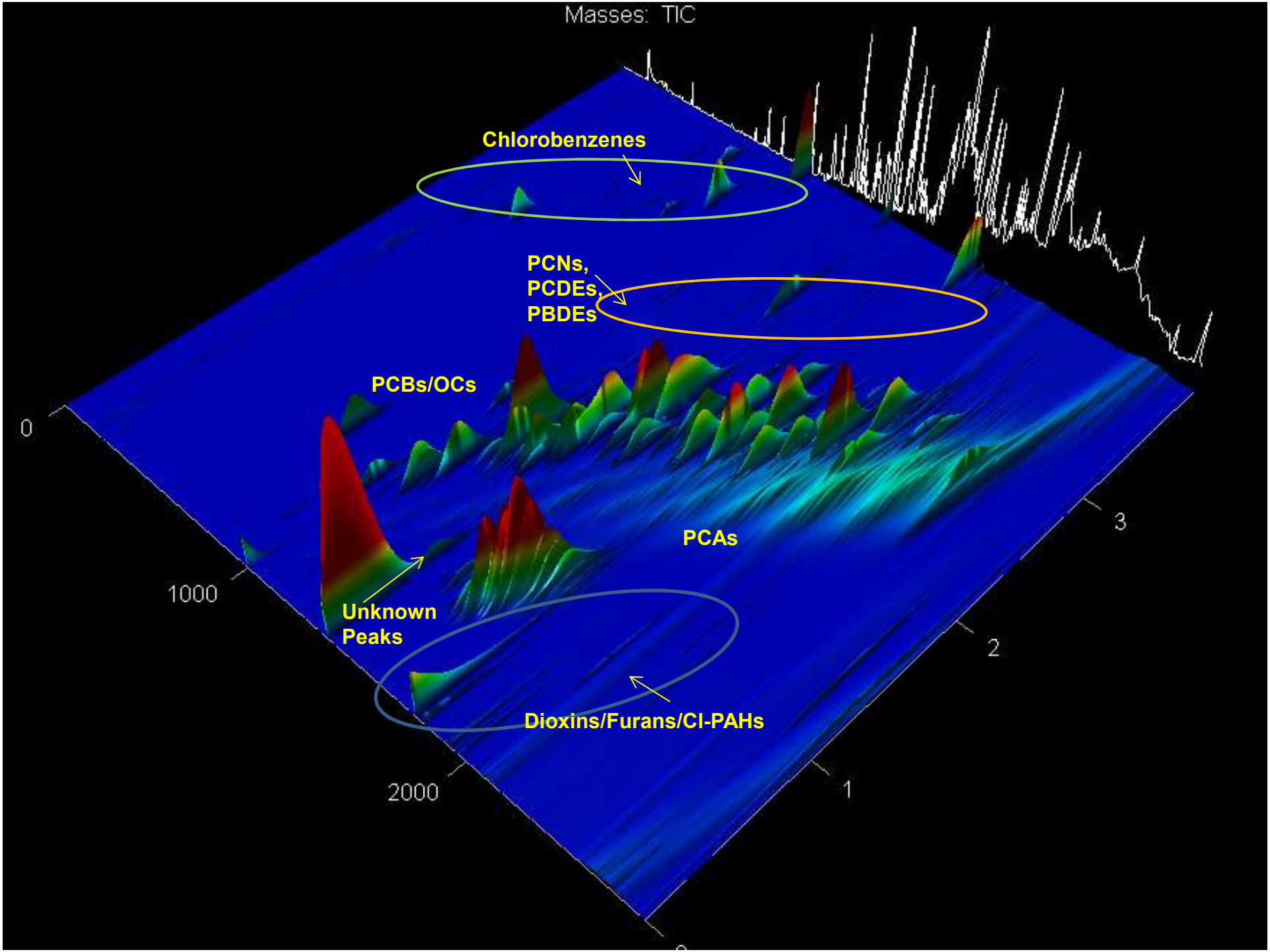
PCB Standard by GC×GC-ECD

Orthogonal Elution

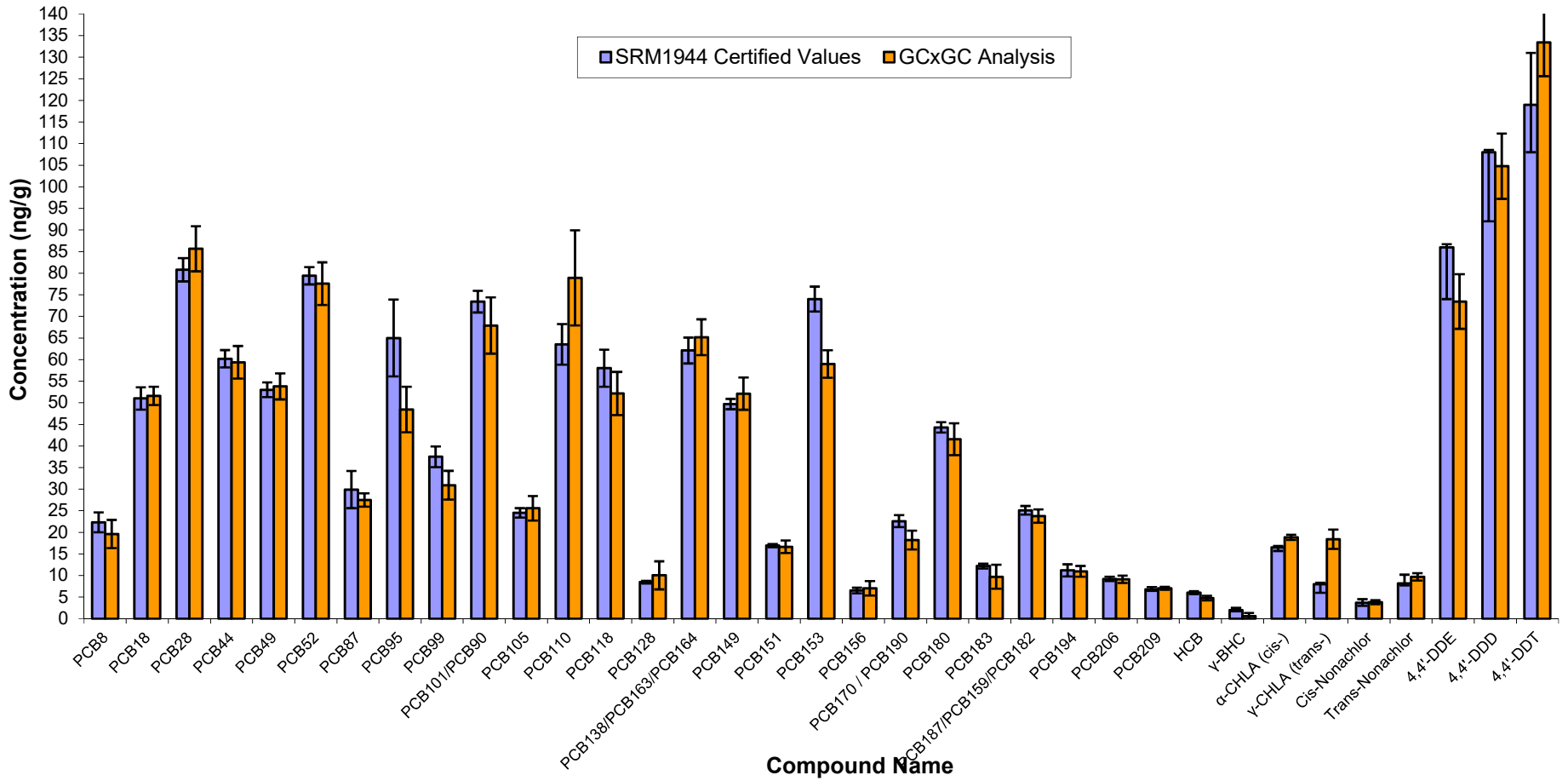


Ontario


Masses: s1
Chlorobenzenes
PCNs, PCDEs, PBDEs
PCBs/OCs
PCAs
Unknown Peaks
Dioxins/Furans/Cl-PAHs
748
1248
1748
2248
3.06
2.06
1.06


Masses: TIC
Chlorobenzenes
PCNs,
PCDEs,
PBDEs
PCBs/OCs
PCAs
Unknown
Peaks
Dioxins/Furans/Cl-PAHs
0
1000
2000
3
2
1

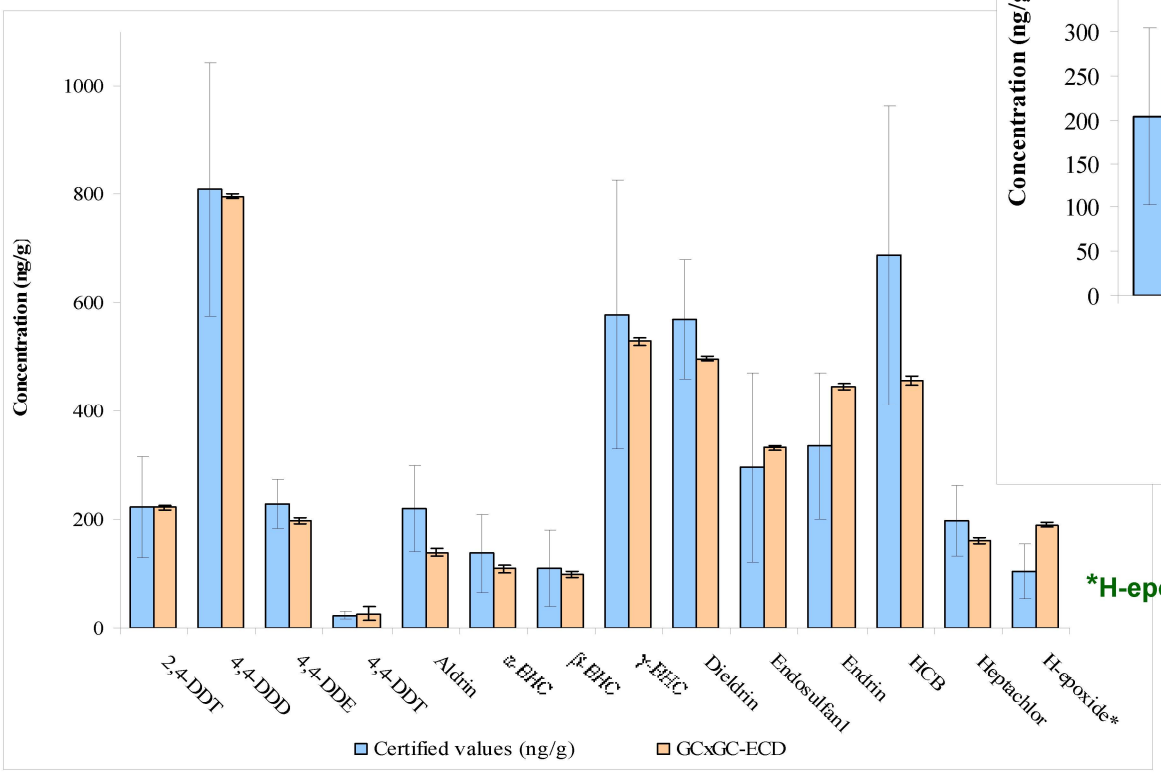
SRM1944 Analysis – Within Run (n=10)

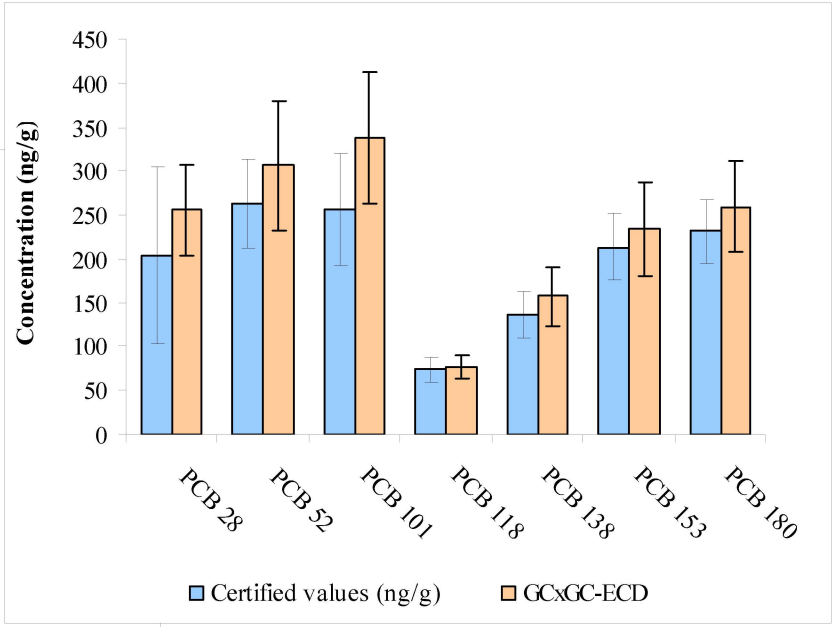


Ontario

CNS312 – Sludge Reference Material

Data comparison for selected PCBs and OCs in CNS312



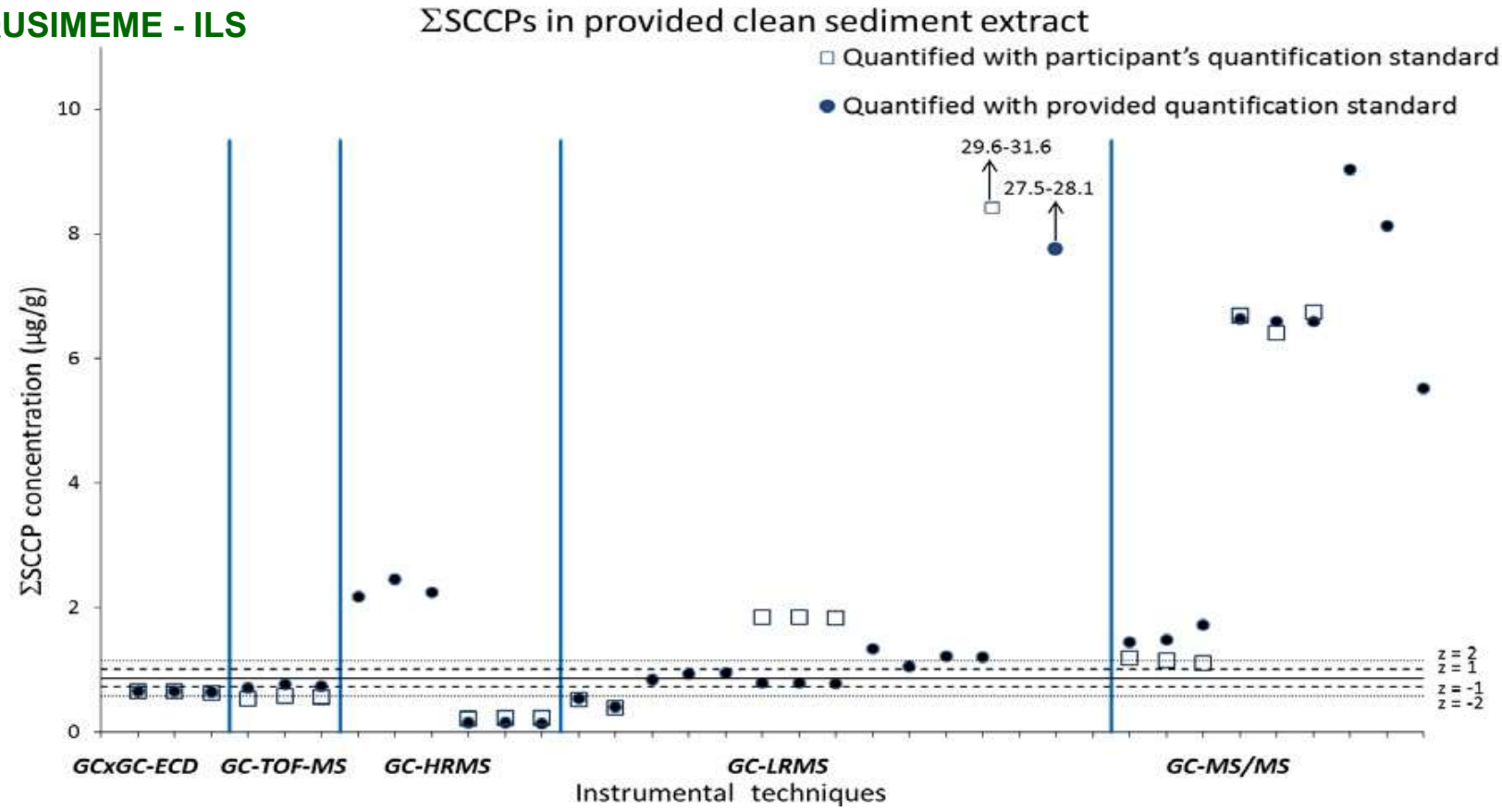


***H-epoxide coelution with PCB74**

Ontario

Short Chain Chlorinated Paraffins SCCPs

QUSIMEME - ILS

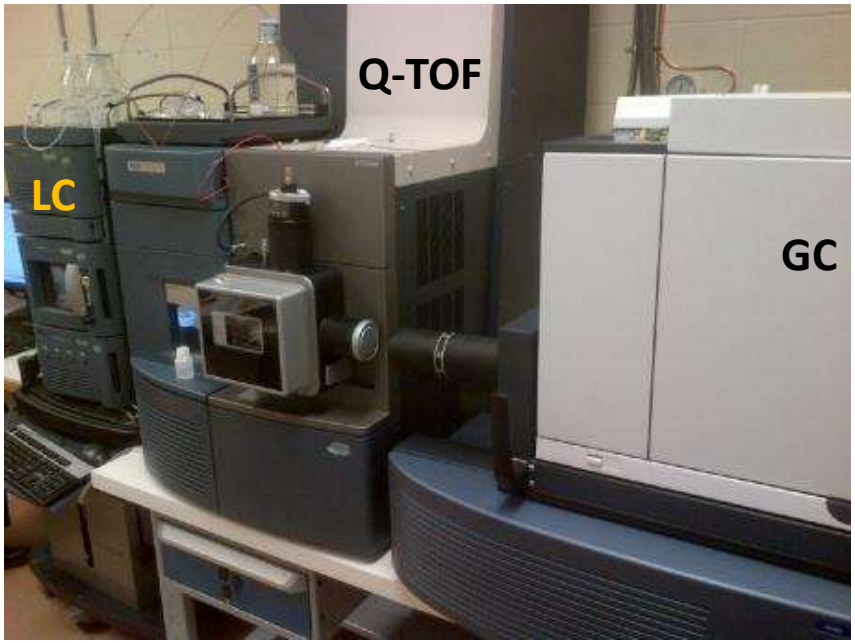


Also identified as Polychlorinated Alkanes - PCAs

Ontario

The Universal Mass Spectrometry System

Waters Xevo G2-XS Q-TOF

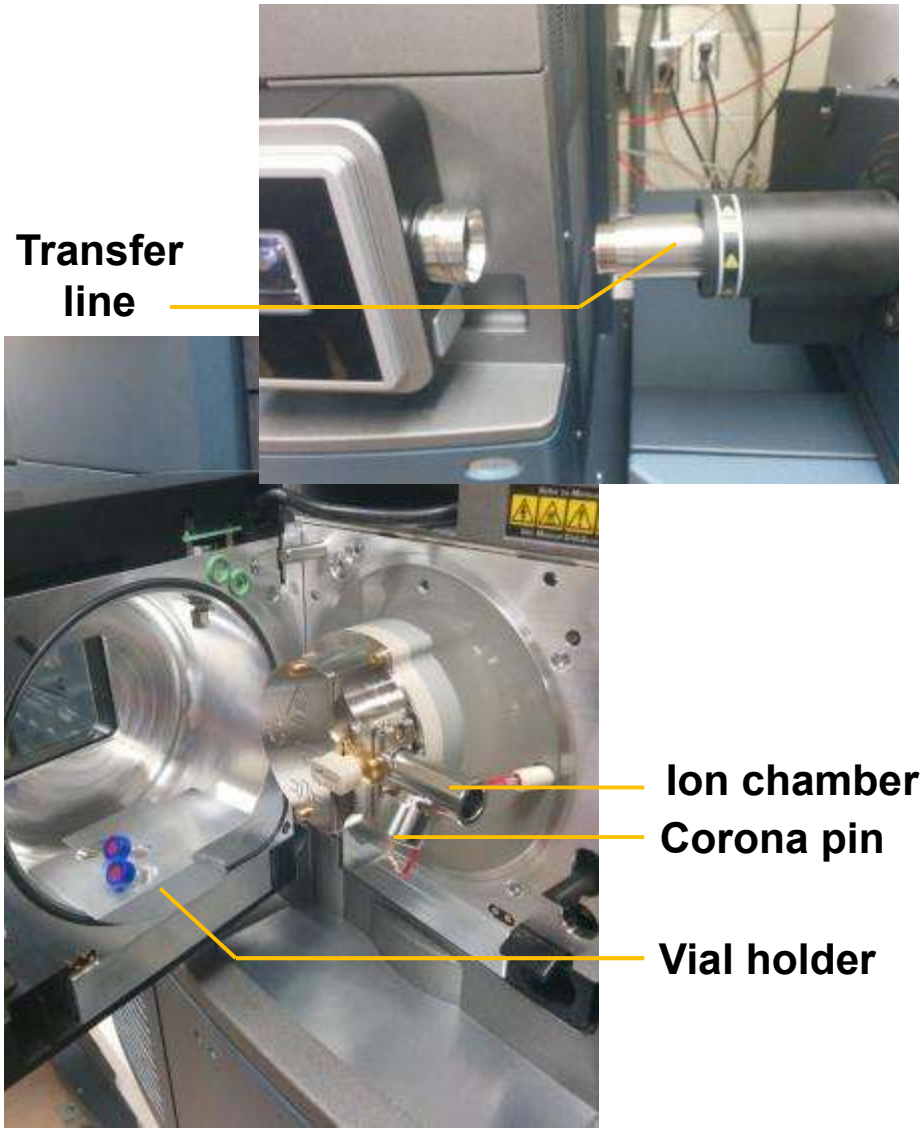


System Attributes

- **Mass range m/z 20 – 4000 (Q-limited)**
  Covers most environmental contaminants
- **Maximum Acquisition rate 30 Hz**
  Capable of LC, GC and GCxGC experiments
- **Mass Resolution 25,000 – 35,000 FWHM**
  Slightly better than an HRMS instrument tuned for dioxin analysis. Enables mass defect analysis.
- **Mass Accuracy < 1mDa**
  That's equivalent to ~2 electrons!
- **Full Scan data acquisition –**
  Can do Target and Non-targetanalysis !

Zoex ZX2 modulator

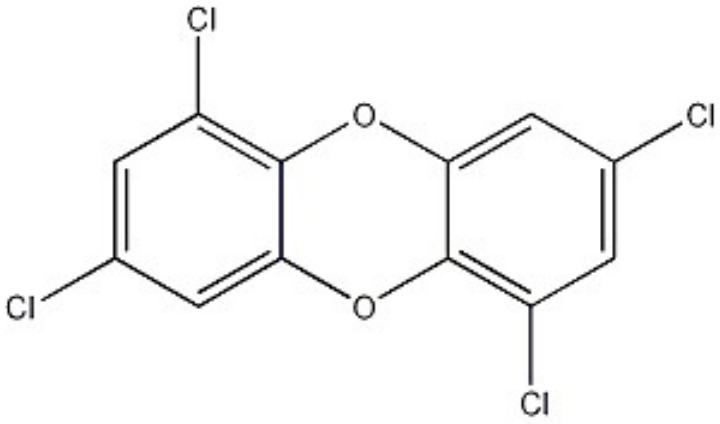
Atmospheric Pressure Gas Chromatography (APGC)



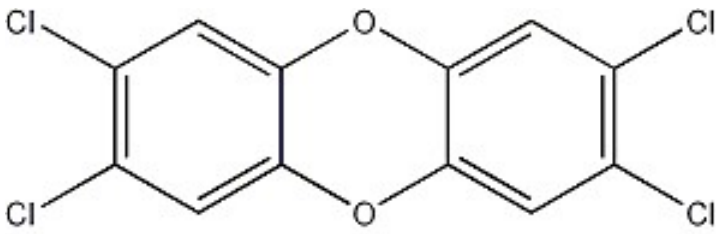
GC inlet and ionization

- Transfer line heated to 300 °C - 360°C
- Corona pin initiates ionization.
- Ionization similar to processes observed for APCI in LCMS
- Positive ionization usually occurs by charge exchange with $N_2^{\bullet+}$.
- H_2O and other gases can be introduced to modify the ionization process. (proton transfer e.g.)
- Negative ions may be generated by electron capture, but other mechanisms may also occur.

Dioxin Toxicity



1,3,6,8 Tetrachlordibenzo-p-dioxin



2,3,7,8 Tetrachlordibenzo-p-dioxin

NOEL = 3g / kg

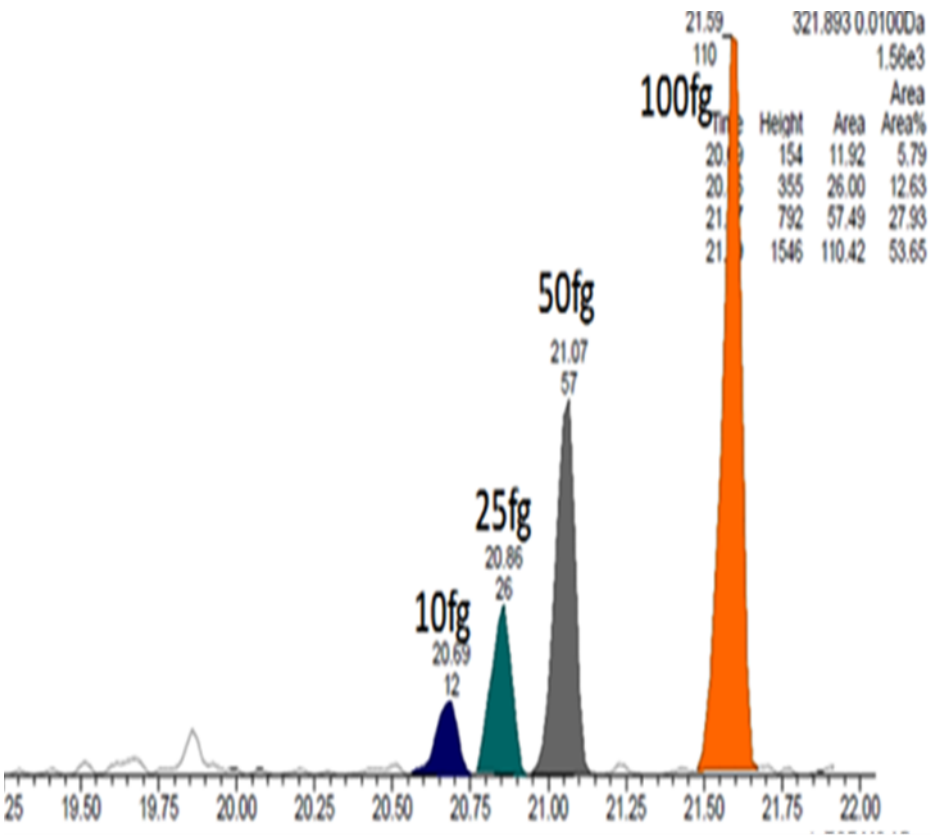
LD_{50} = 1ug / kg

There are 210 Dioxins and Furans. Congeners with chlorines in the 2,3,7, or 8 positions are bioaccumilative and toxic

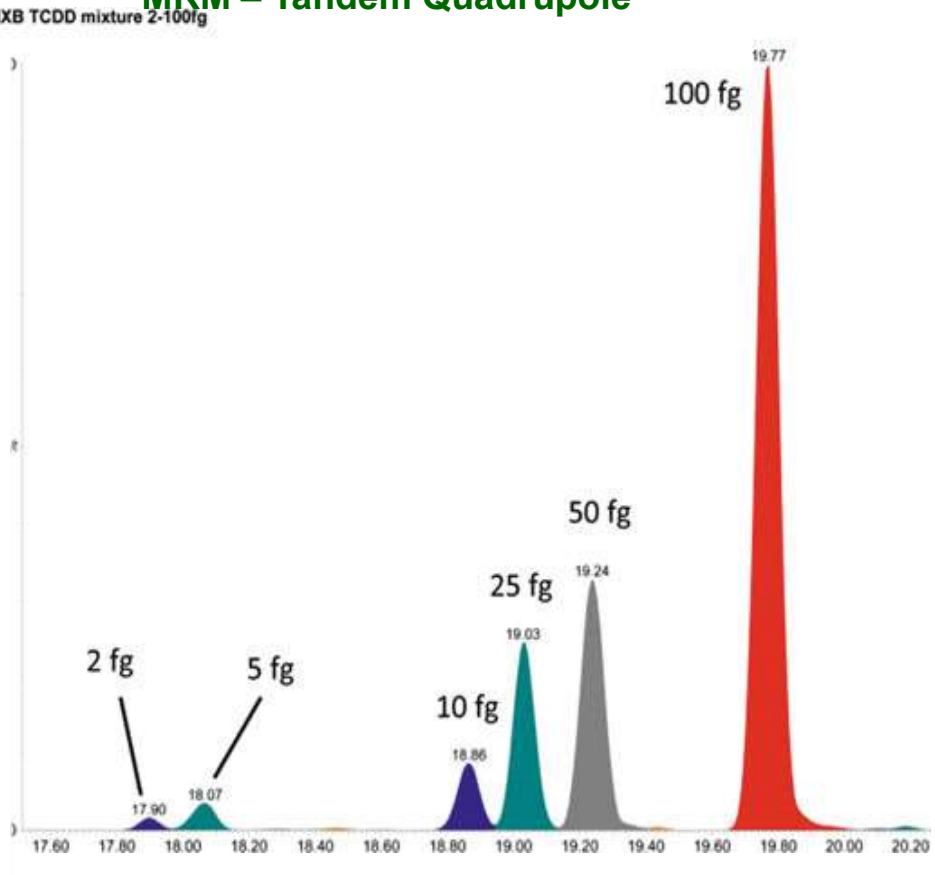
Instrument sensitivity (APGC) - full scan vs MRM

Wellington Dioxin Sensitivity Mix

Full Scan – Q-ToF



MRM – Tandem Quadrupole



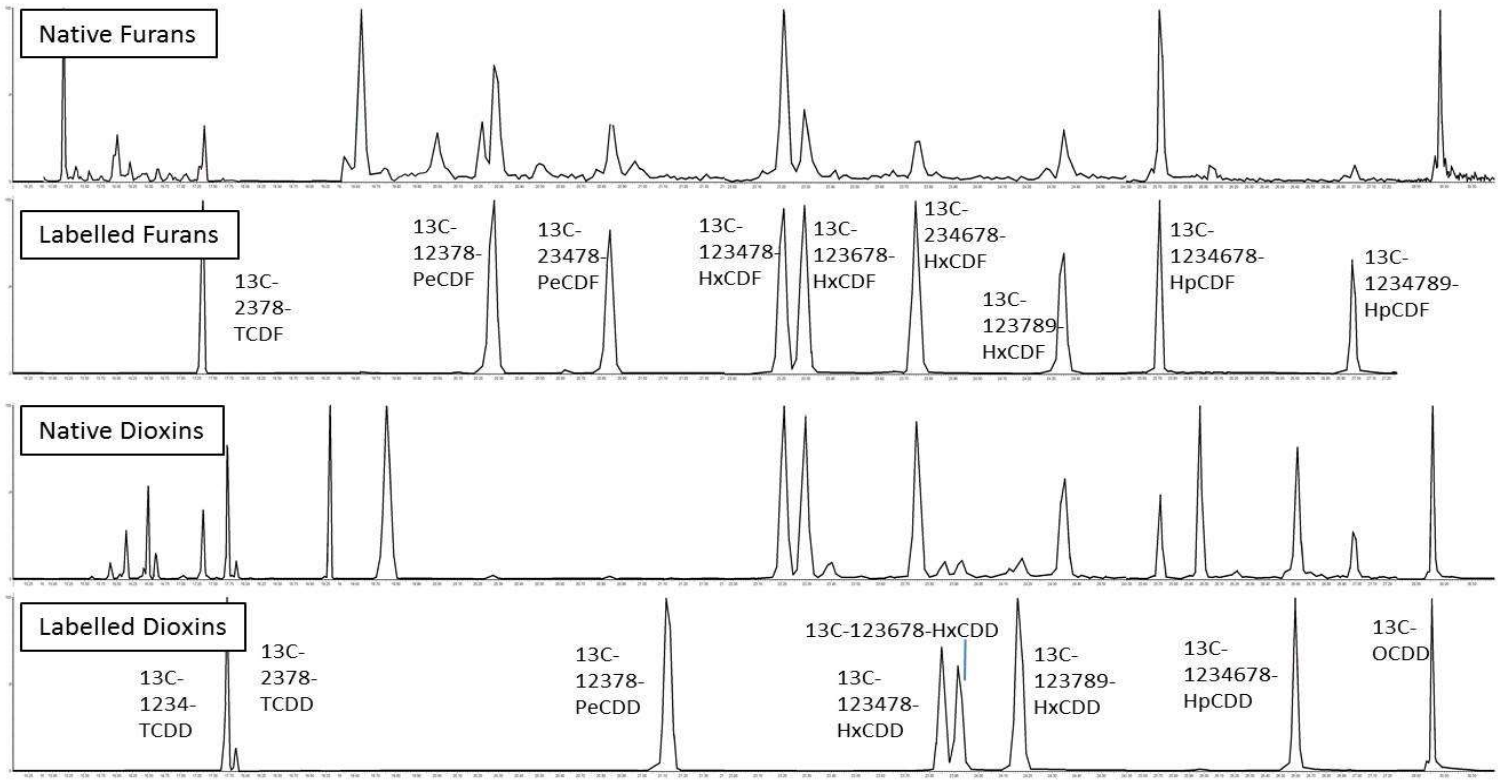
Organtini et al., Anal. Chem. (2015) 87 (15), 7902-7908

QuEChERS for Dioxin in Contaminated Sediments

QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe)

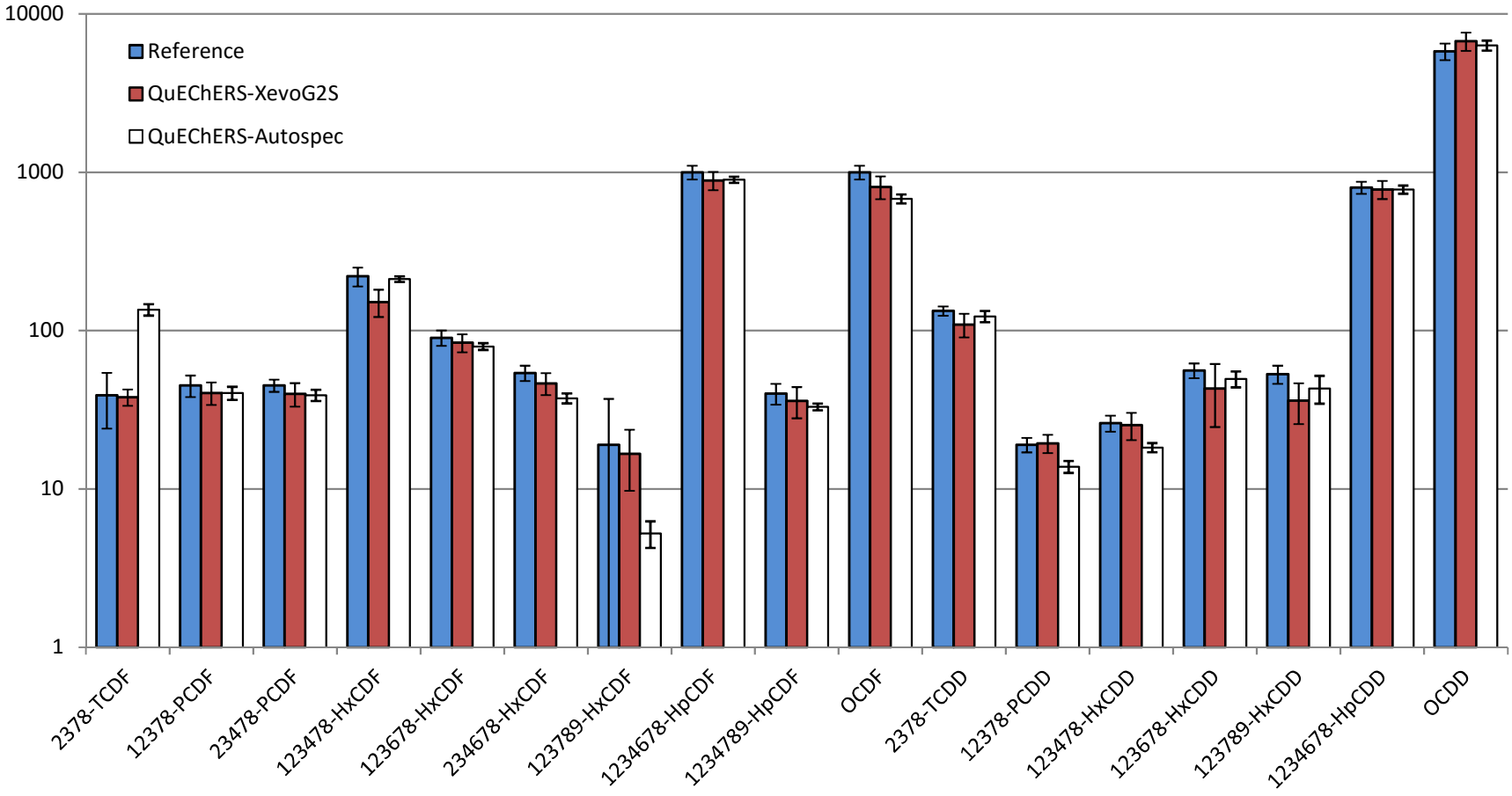
- ACN extraction with mini silica / carbon cleanup
- Detection limits 3 x higher than classical method (EPA 1613)
- Uncertainty ±35% Extract and cleanup 30 samples in 1 day

NIST 1944 – Results compare within 7% HRMS (1613) vs QuEChERS – N=10



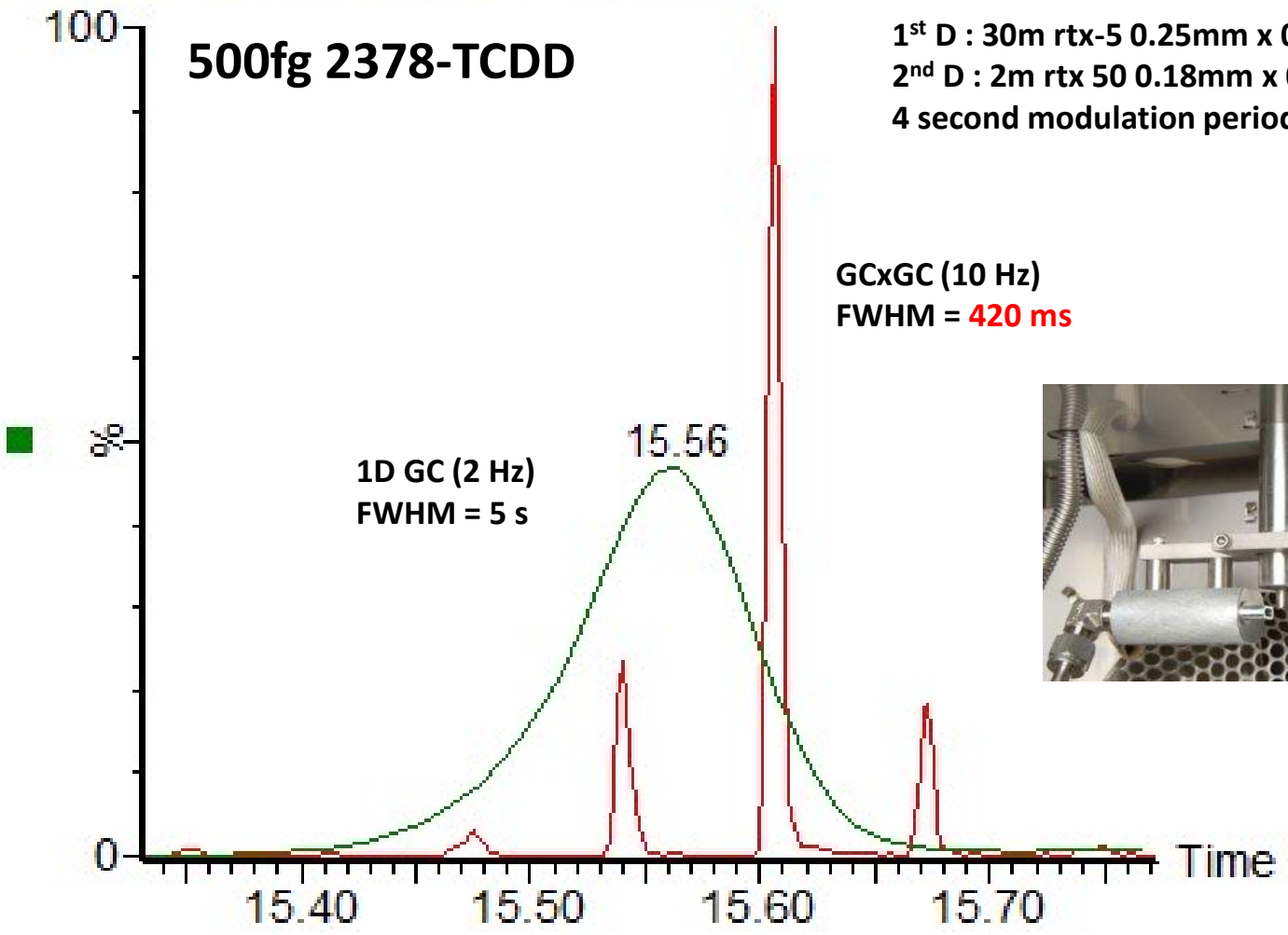
Richman et al, J Environ. Protection, 7, 453-466 (2016), Haimovici et al, Anal Bioanal Chem Accepted (2016).

Comparison of NIST1944

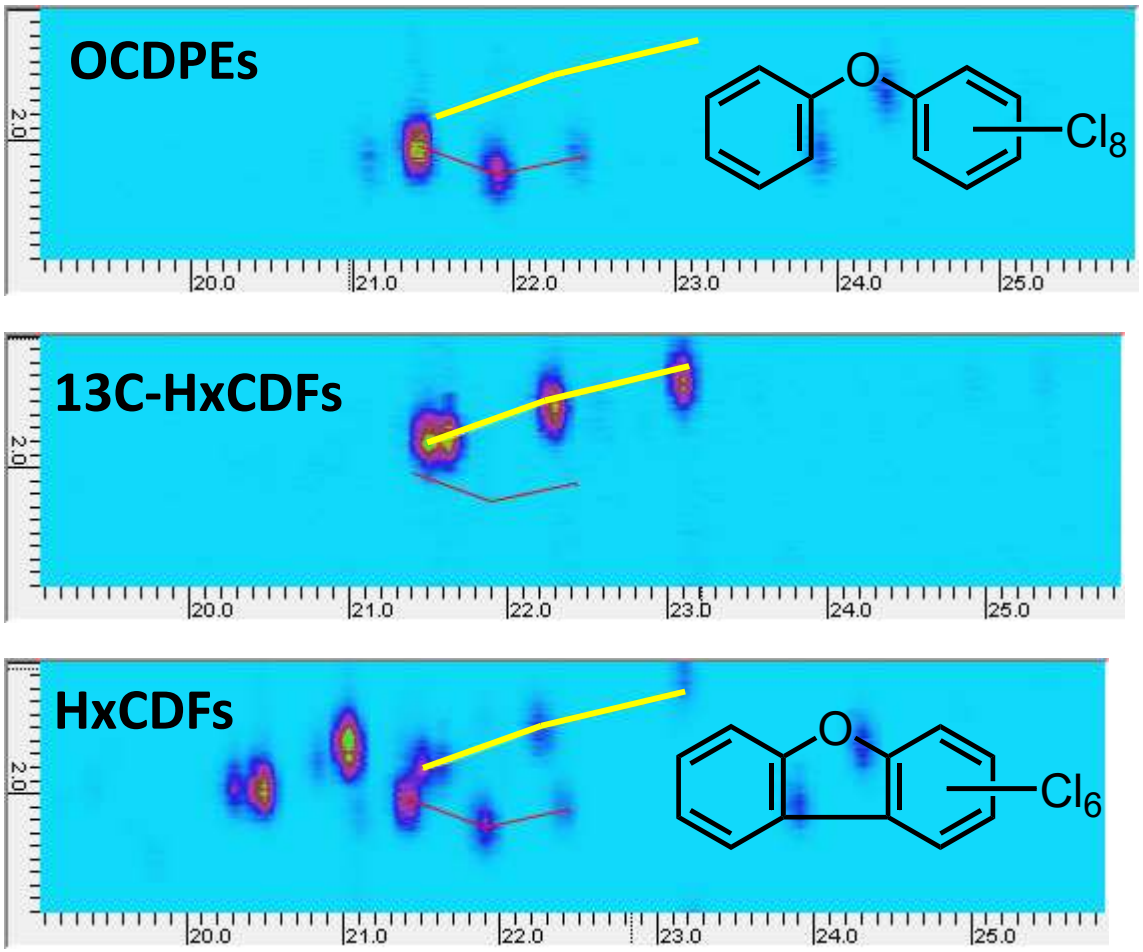


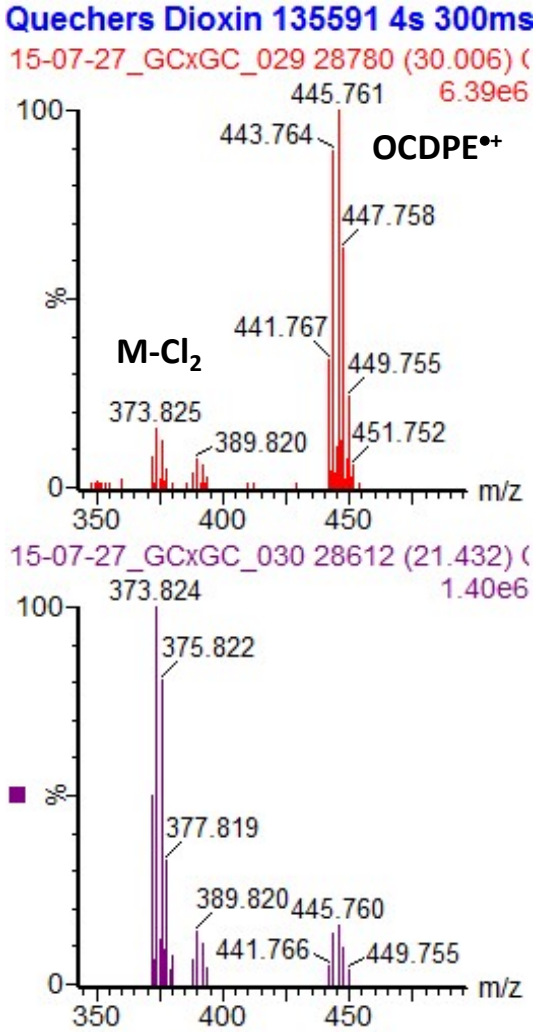
Certified TEQ: 243.0 pg
QuEChERS-XEVO TEQ: 204.9 pg (15.7% Difference)
QuEChERS-Autospec TEQ: 226.7 pg (6.7% Difference)

GC×GC can enhance sensitivity



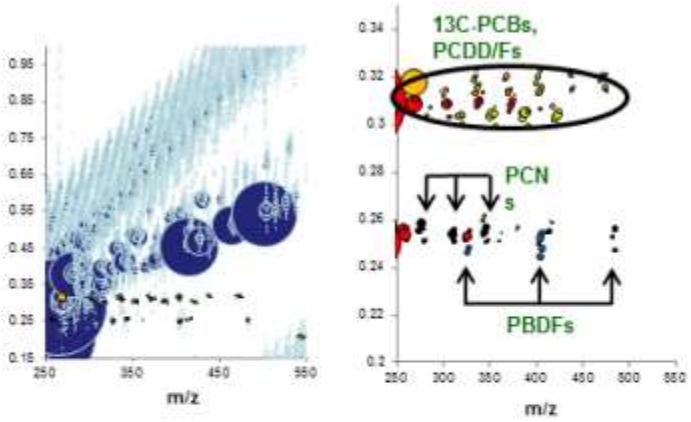
APGC reduces interferences and GC×GC can resolve them



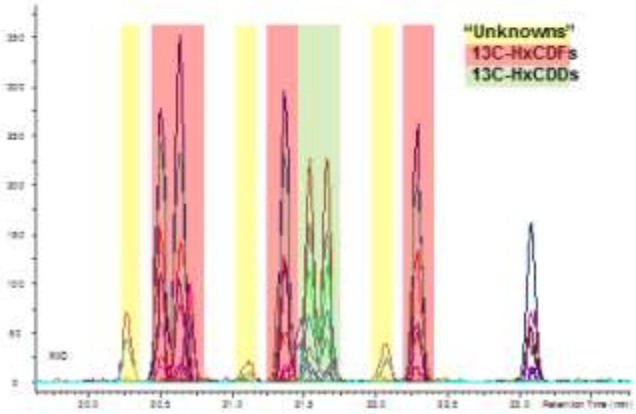


Goal : a routine, automated, non-targeted analysis

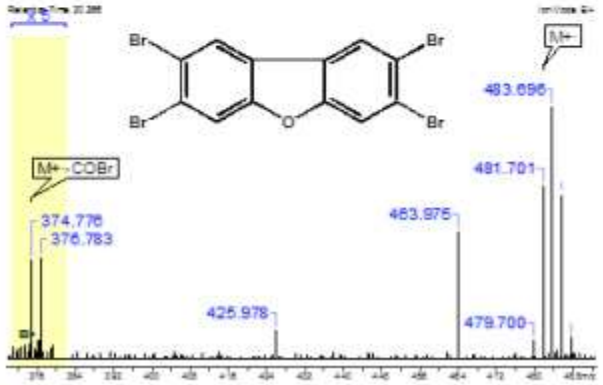
(1) Mass defect filtering reveals halogenated ions



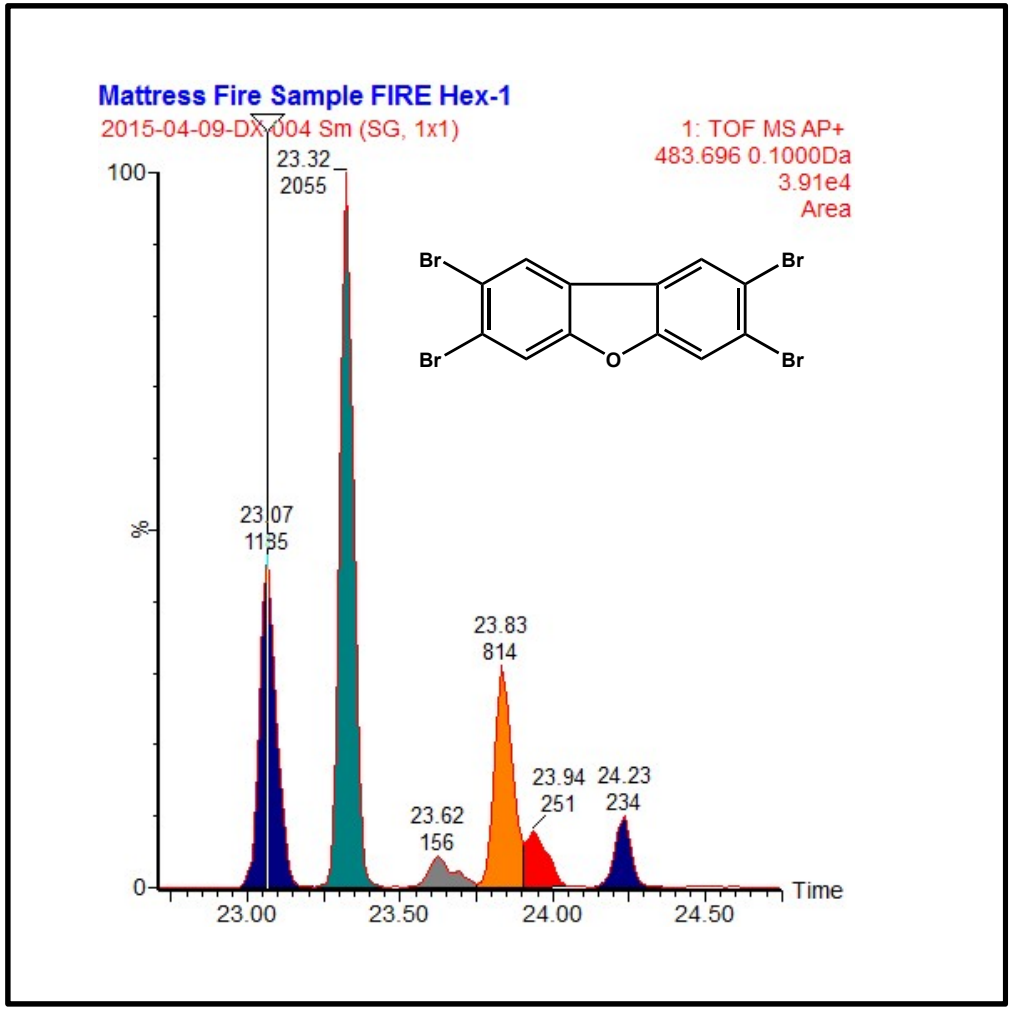
(2) Software deconvolution of both target *and* non-target compounds.

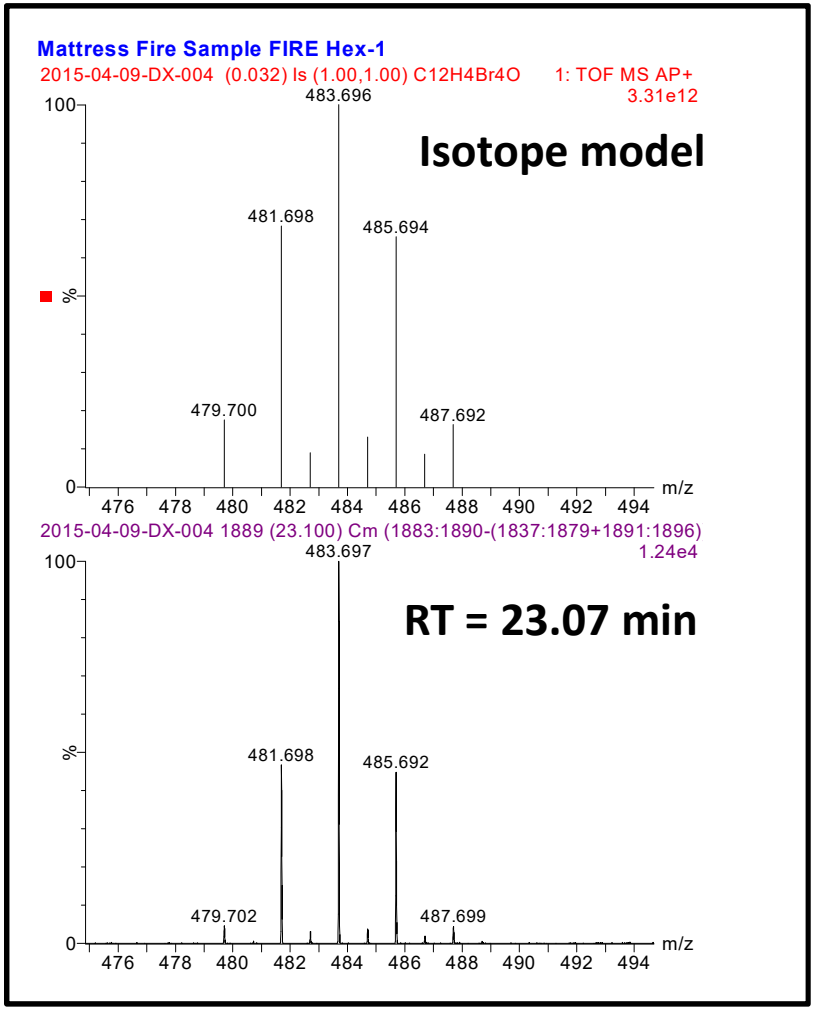


(3) Interpretation of full-scan high resolution mass spectra leads to structure proposal :



Target and non-target analysis in a single injection





The TEQ is increased 10x when 2,3,7,8-TBDD/F are included!

Conclusions

- Certified reference materials are the ultimate tool for determining tractability and method performance and validation
- They provide the best results for data comparison and conflict resolution
- They often contain and can be used to identify new environmental contaminants
- More CRMs are required for POPs analytical methods
- There is a need to have more parameters identified and certified

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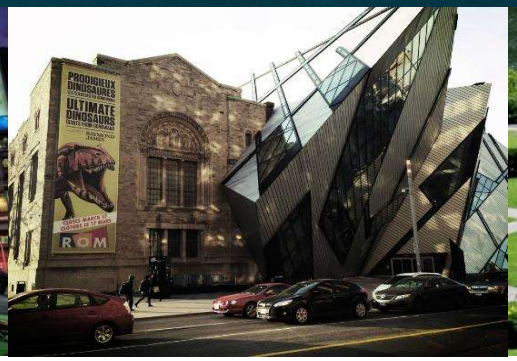
Thank you for your attention!



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- 2016-05-15: Early Registration End
- 2016-08-20: Short Courses Start
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