

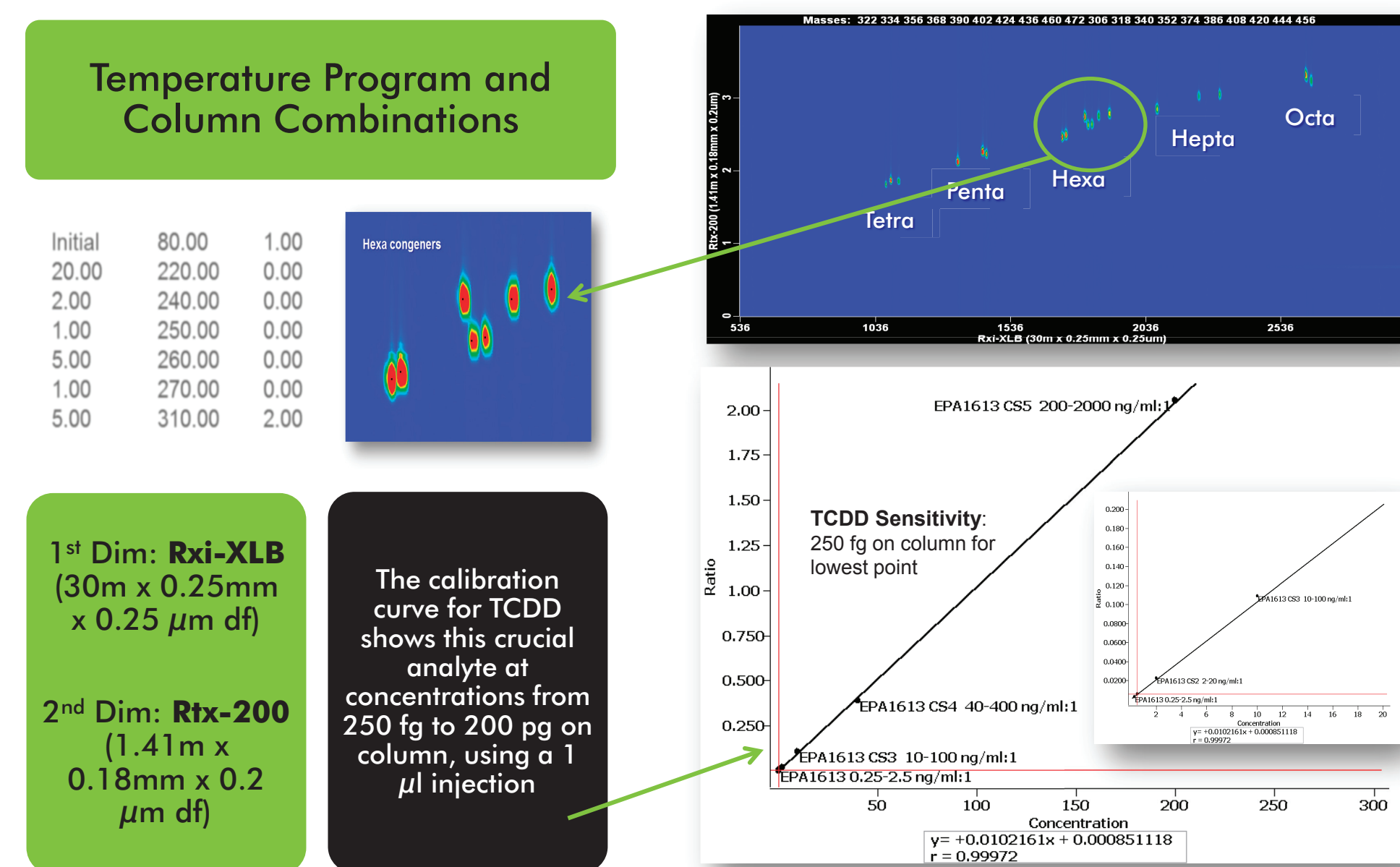
Persistent Organic Pollutant (POP) Analysis in Developing Countries: Refinement and Confirmation of GCxGC-TOFMS Technology

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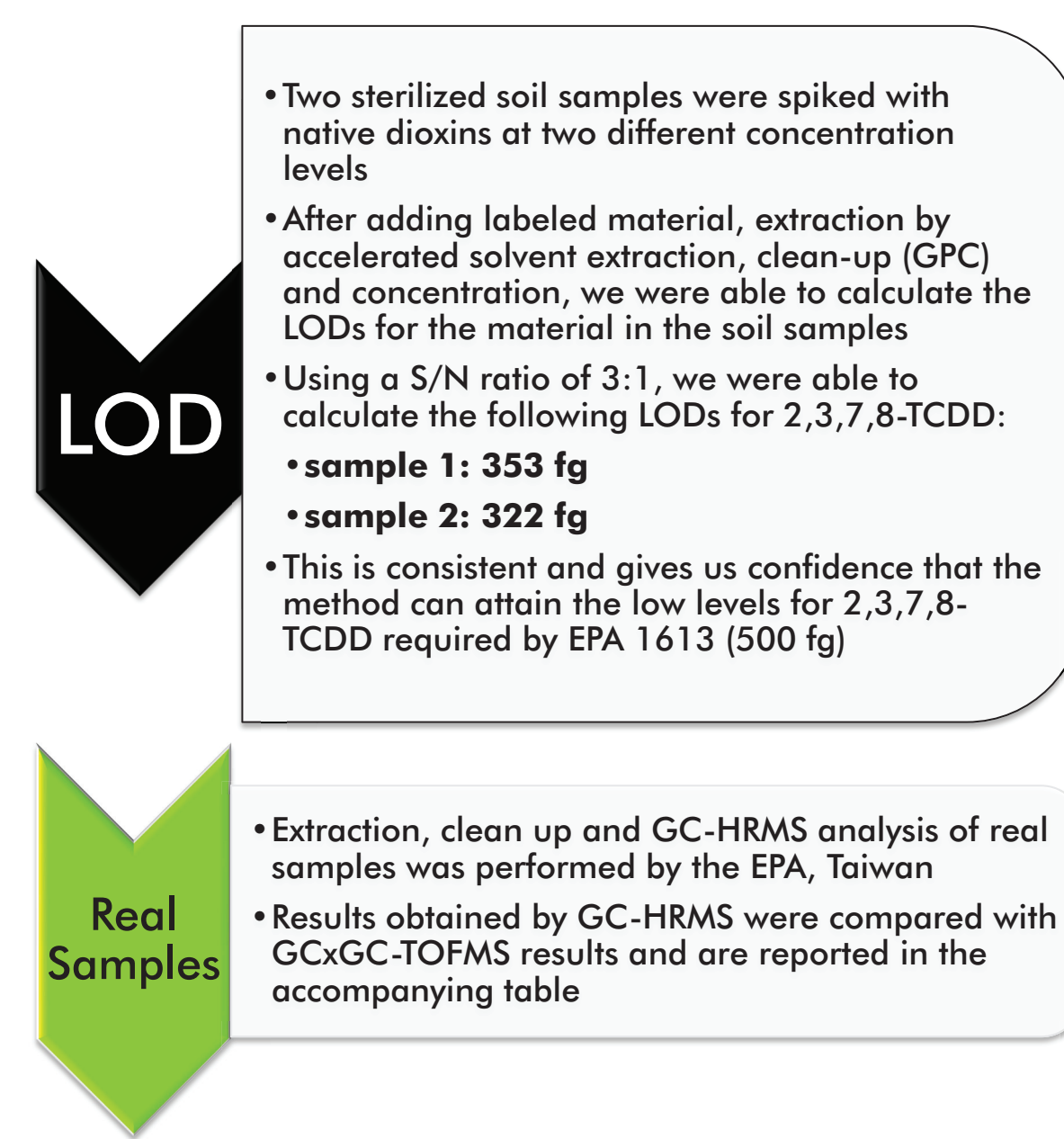
Introduction

South Africa, as with many developing countries, has no established GC-HRMS facilities for dioxin analysis. A need exists to develop an alternative solution which is affordable, easy to manage, and aligned to the country's needs. The resultant analytical approach must be robust, must provide fast turnaround times, and must screen for many classes of environmental pollutants (POPs) in a single analysis. GCxGC-TOFMS provides enhanced **selectivity** through the added peak capacity of GCxGC, and the necessary **sensitivity** through the focusing effect of the modulator. It is **NOT** a target molecule technique (such as SIM), so it is ideal for the screening for multiple compound classes.

Sensitivity and Selectivity



LOD and Analytical Results



Sample Results Table

	Sample 1 (fly ash)		Sample 2 (sediment)		Sample 3 (sediment)		Sample 4 (standard, no extraction)	
	*TOF	⁴ HRMS	*TOF	⁴ HRMS	*TOF	⁴ HRMS	*TOF	⁴ HRMS
2,3,7,8-TCDD	3.2	2.6	16	13	68	73	65	69
1,2,3,7,8-PeCDD	14	16	69	78	4.3	4.8	4.1	4.5
1,2,3,4,7,8-HxCDD	14	13	6.8	6.6	6.5	7.6	0.6	0.7
1,2,3,6,7,8-HxCDD	17	16	8.4	8.0	14	14	1.3	1.3
1,2,3,7,8,9-HxCDD	12	9.4	6.0	4.7	10	11	1.0	1.0
1,2,3,4,6,7,8-HpCDD	123	77	6.1	3.8	197	124	1.9	1.1
OCDD	283	240	0.1	0.1	1000	940	0.1	0.1
2,3,7,8-TCDF	25	21	12	11	47	47	4.4	4.5
1,2,3,7,8-PeCDF	43	46	11	11	20	14	0.9	0.8
2,3,4,7,8-PeCDF	107	129	270	320	215	246	102	116
1,2,3,4,7,8-HxCDF	93	100	46	48	217	235	20	22
1,2,3,6,7,8-HxCDF	105	105	52	52	21	17	2.0	1.6
2,3,4,6,7,8-HpCDF	197	174	98	86	20	16	1.9	1.5
1,2,3,4,7,8,9-HpCDF	32	29	16	14	8.1	6.7	0.8	0.6
1,2,3,4,6,7,8,9-HpCDF	400	412	20	21	670	740	6.3	7.0
OCDF	58	48	2.9	2.4	17	13	0.2	0.1
TOTAL PCDD/Fs	232	266	0.1	0.1	850	920	0.1	0.1
	640	680			210	230		

HR-GCMS results provided courtesy of Dr Peng, EPA, Taiwan, using the 1998 World Health Organization (WHO) Toxicity Equivalency Factor (TEF) values

*TOF: GCxGC-TOFMS results (pg/µl), ⁴HRMS: GC-HRMS results (pg/µl)

*TOF TEF: GCxGC-TOFMS TEQ results calculated per weight of sample extracted (ng WHO TEQ.kg⁻¹), ⁴HRMS TEF: GC-HRMS TEQ results (ng WHO TEQ.kg⁻¹)

GCxGC-TOFMS in Environmental Forensic Work

GCxGC-TOFMS is unique in that it is the only technique which has the ability to analyze complex samples and evaluate all the components at the levels needed for POP determination in one analysis. As such it can fill an extremely important role in the preliminary screening of environmental samples, providing rapid and comprehensive determination of whether a sample contains components harmful to human and animal health.

An investigation was conducted at a waste disposal facility suspected of dumping toxic waste into the environment. Three samples were taken at different locations, and submitted for analysis. The samples were screened for numerous POPs. We shall examine results for one sample only.

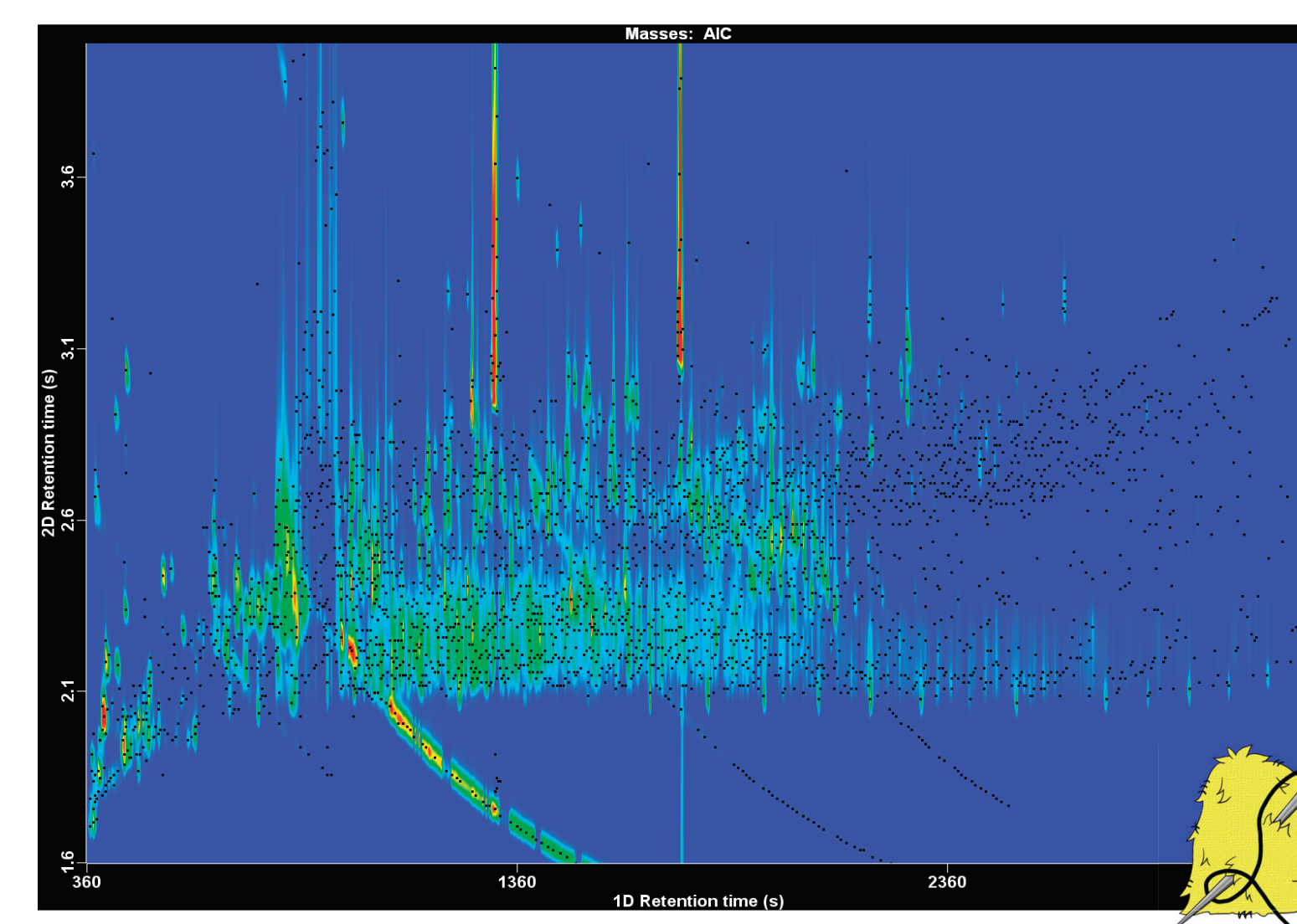
Sample Preparation

Sample extraction and purification was done by Prof. Jef Focant at the University of Liege, Belgium. A 1 gram portion of sample was Soxhlet extracted with toluene. Solvent exchange to hexane was performed followed by chromatography on a multilayer silica column (AgNO₃, 22% acid, 44% acid, basic). The final concentrated extract was then passed through a Pasteur pipette type acidic silica column prior to injection. Samples were analysed by GCxGC-TOFMS (South Africa) and GC-HRMS (Belgium).

Analytical Conditions for GCxGC-TOFMS

GCxGC	TOFMS
First Dimension Column	Rtx-5SIMS (30 m x 0.25 mm id x 0.25 µm df)
Second Dimension Column	Rtx-PCB (1.1 m x 0.18 mm id x 0.18 µm df)
Carrier Gas	Helium
Injection Mode	Splitless
Injection Volume	2 µl
Flow Mode	Corrected constant flow via pressure ramps
Flow Rate	1.00 ml/min
Inlet Purge Time	60 s
Inlet Temperature	250°C
First Dimension Column Temperatures	140°C for 1 min, ramp at 20°C to 180°C, no hold, then at 3°C to 295°C, hold for 3.67 min
Second Dimension Column Temperatures	160°C for 1 min, ramp at 20°C to 200°C, no hold, then at 3°C to 315°C, hold for 3.67 min
Transfer Line Temperature	270°C
Modulation Period	5 s
Acquisition Delay	600 s
Start Mass	100u
End Mass	520u
Acquisition Rate	50 spectra/s
Detector Voltage	1950V
Electron Energy	-80V
Mass Defect Setting	-40 mu/100u
Ion Source Temperature	250°C

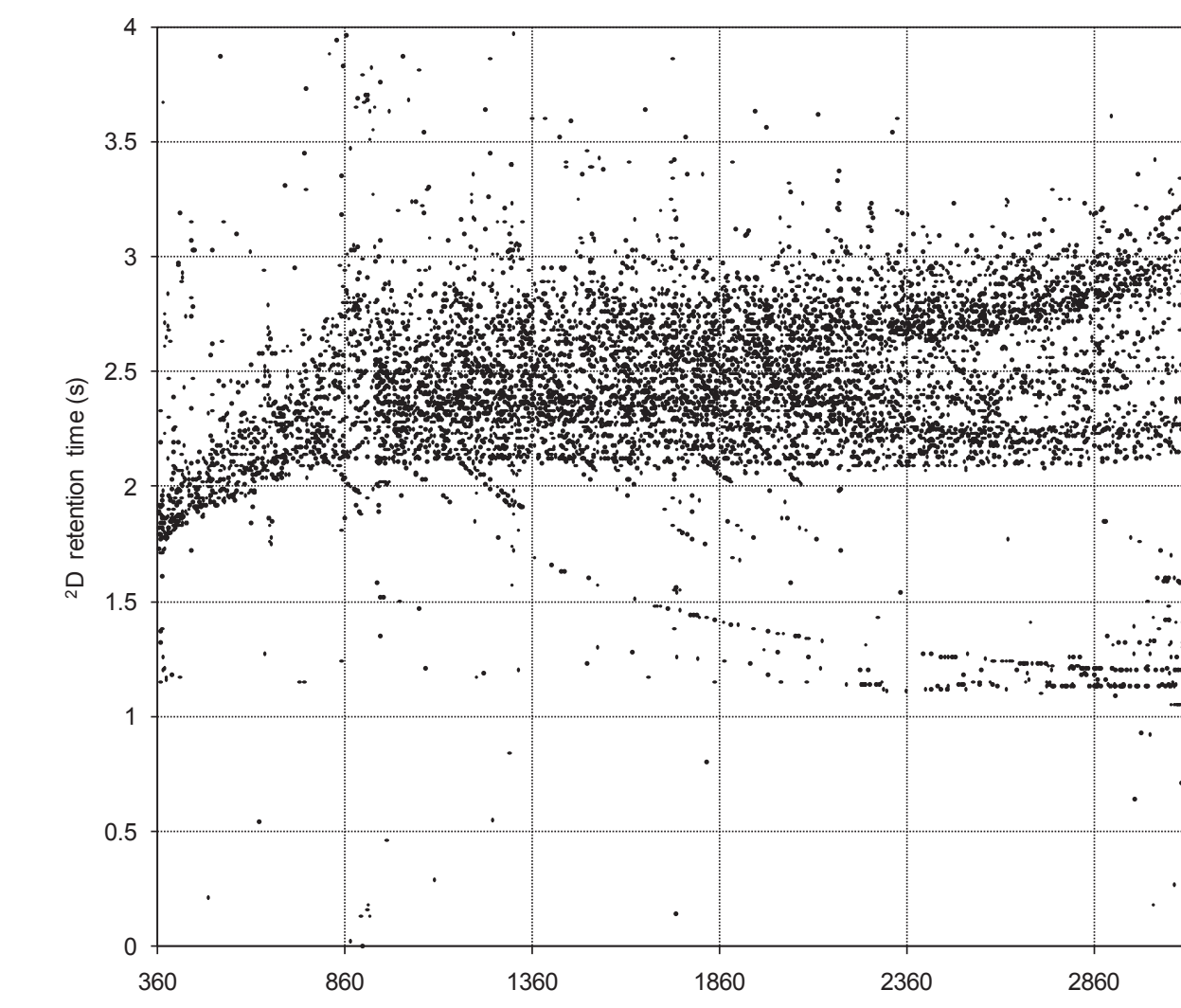
GCxGC-TOFMS Chromatogram



The software locates more than 7000 components in the sample. We need to identify possible pollutants among all the other components (mostly matrix) present. We need to find the diamonds in the dirt!

An Apex plot of the results obtained in the above GCxGC-TOFMS chromatogram simplifies the visual complexity of the chromatogram, and after applying scripting, it is then easier to present a visual picture of some of the priority pollutants present in these complex environmental samples as depicted in the accompanying diagrams.

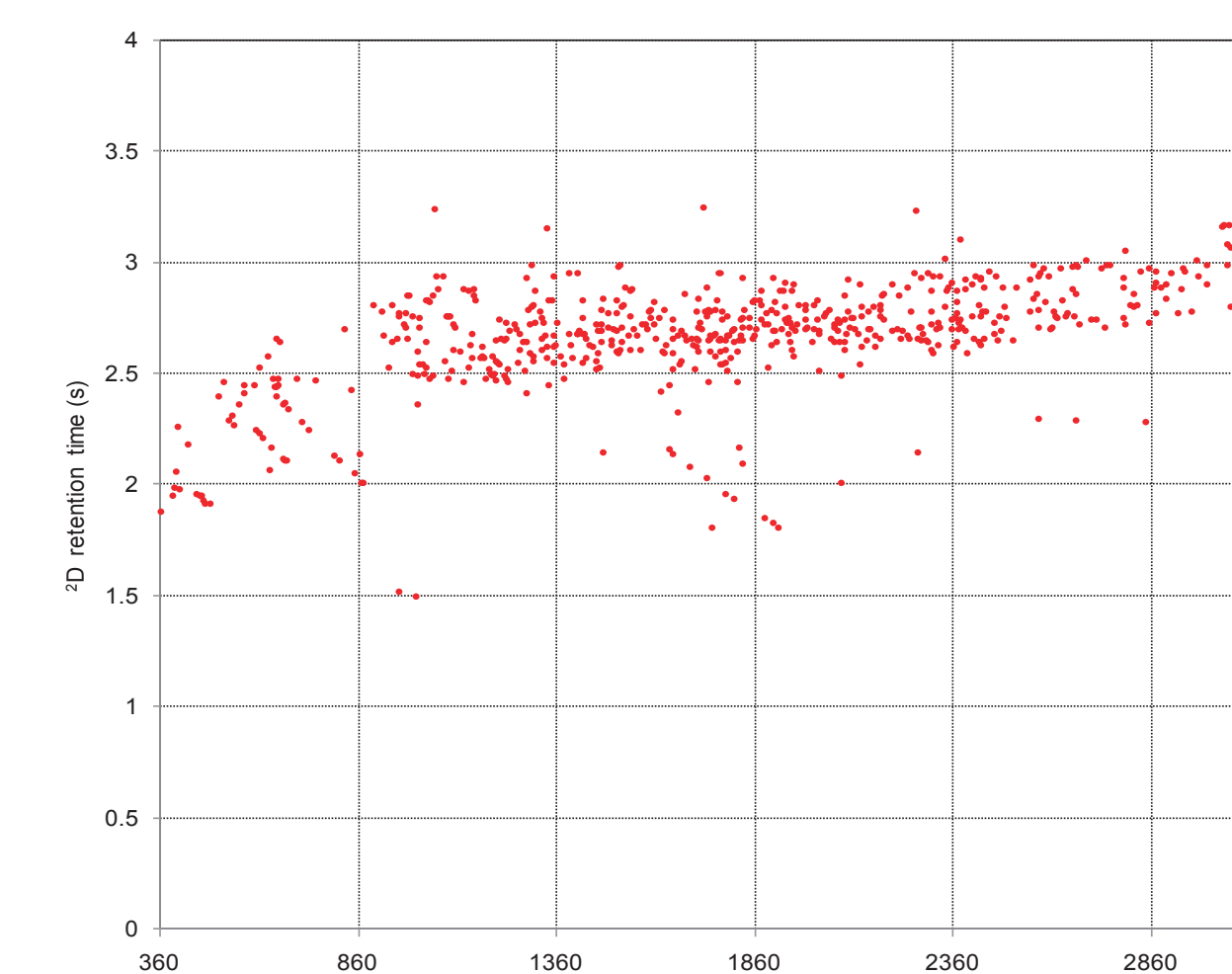
Apex Plot of the Components in the Sample



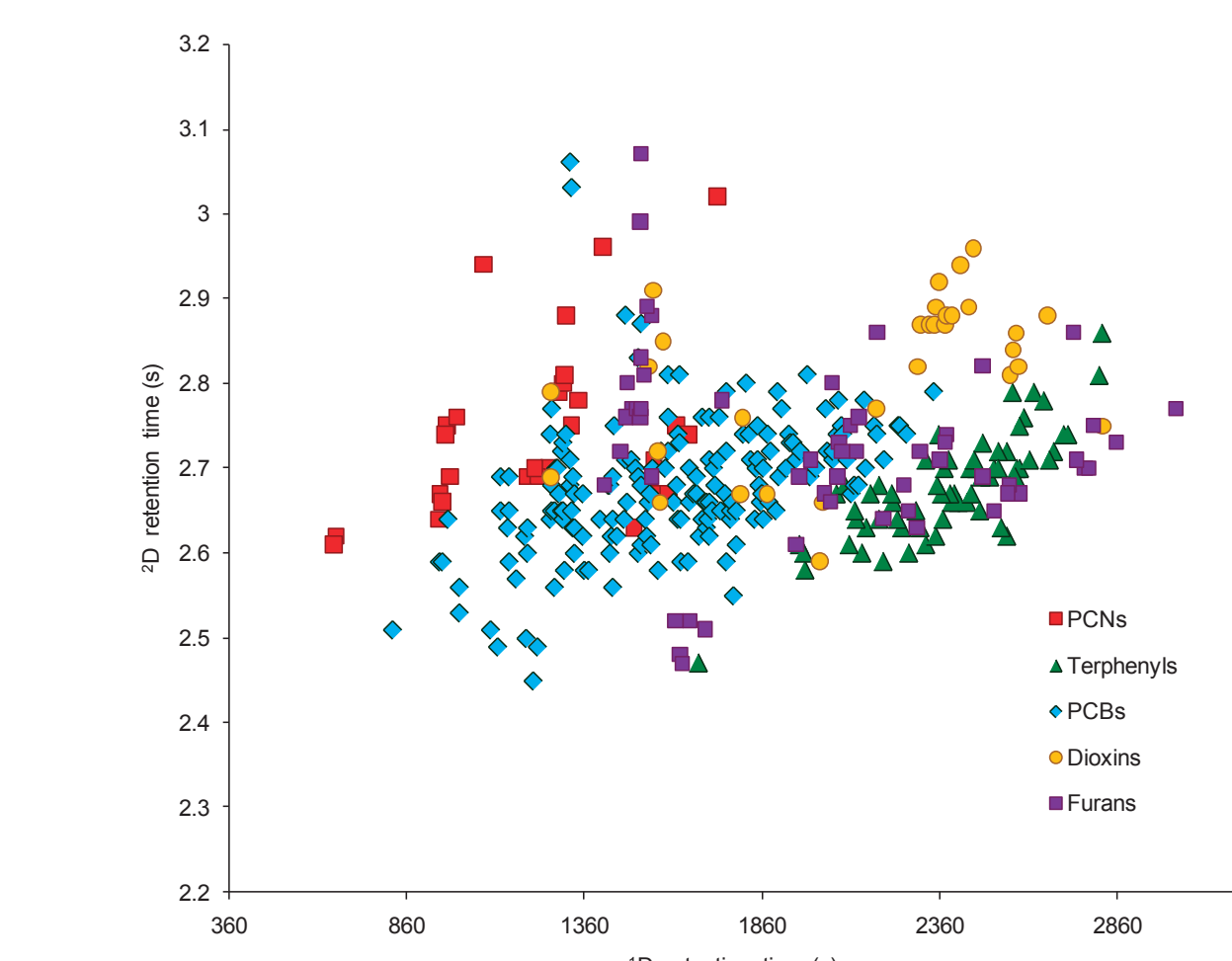
Scripting

The ChromaTOF[®] scripting software uses Microsoft VB script language to write functions that define compounds of interest using mass spectral criteria. So we can use the scripts to filter data in a sample to locate only those compounds we are interested in. The process is ultra fast, and can save large amounts of time for complex samples. As we are looking for environmental pollutants, many of which contain chlorine, we can apply a script which searches for chlorinated compounds only.

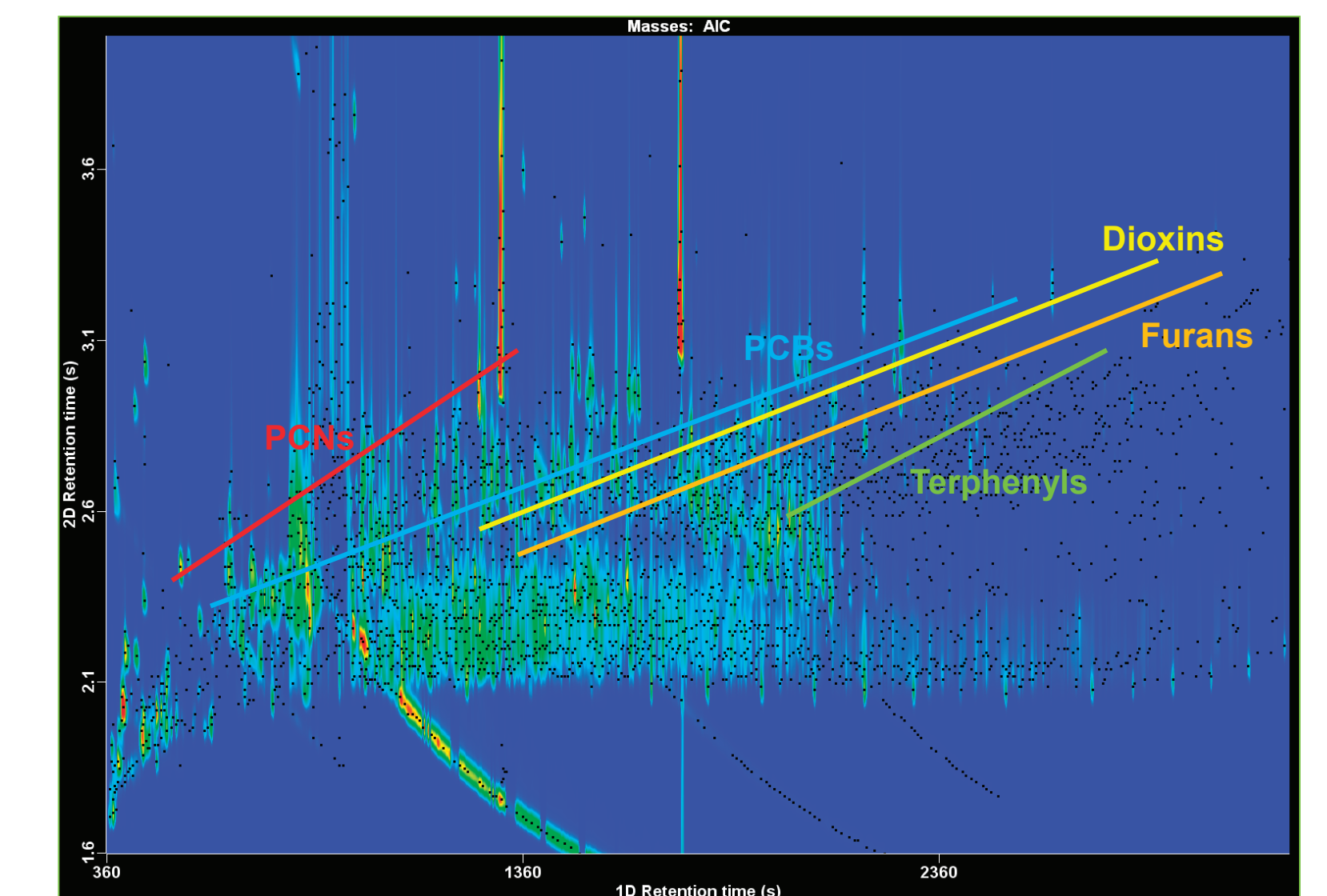
Chlorinated Components Located Using Scripting



Some Priority Pollutant Classes in the Sample



Some Priority Pollutants Shown on the Chromatogram



Conclusions

- GCxGC-TOFMS is a viable tool for dioxin screening and quantitation, especially in cases where PCDD and PCDF levels are > 1 ppb (environmental applications)
- The technique is probably not applicable to biological work at much lower levels (< 250 fg/µl)
- The Rxi-XLB:Rtx-200 column combination provides excellent separation of the compounds mandated for analysis by EPA 1613, provided careful temperature programming is implemented
- ChromaTOF software provides many features useful for dioxin analysis
- The GCxGC-TOFMS methodology has been tested on many real world samples (only some of the results are shown here)
- In the cases where GC-HRMS results were available, a comparison of results between the two technologies revealed very good agreement
- The method can be used as a general POP screen, even in extremely complex environmental samples, and is capable of locating PCDDs, PCDFs, PCBs, PAHs, and numerous other POP compound classes in one run
- The method also meets the isomer specificity criteria as detailed in EPA Method 1613
- Window defining parameters have been achieved with the EDF-4147 standard test sample

Acknowledgments

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References

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- de Vos J, Dixon R, Vermulen G, Gorst-Allman P, Cochran J, Rohwer E, Focant J-F. (2011); *Chemosphere* 82: 1230 - 1239