LECO

EMPOWERING RESULTS

BOOSTING NON-TARGETED ANALYSIS WITH COMPREHENSIVE TWO-DIMENSIONAL GAS CHROMATOGRAPHY AND HIGH-RESOLUTION MASS SPECTROMETRY

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THE Multidimensional Chromatography Workshop

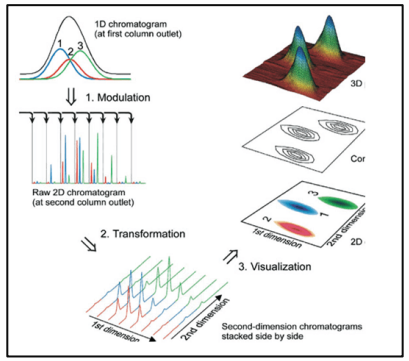
Outline

- Aims
- Samples
- Instrumentation
  - GC×GC-HR-TOFMS
- Results
- Conclusions

1.Demonstrate the benefits of ***GC×GC*** *for Non-Target screening*

2. The role of ***HR-TOFMS*** *and different ionization modes in Non target Analysis*

Assess environmental contamination in the Artic region



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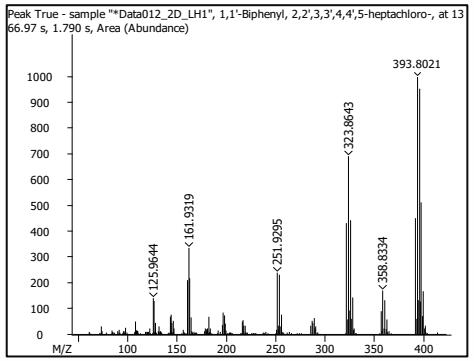

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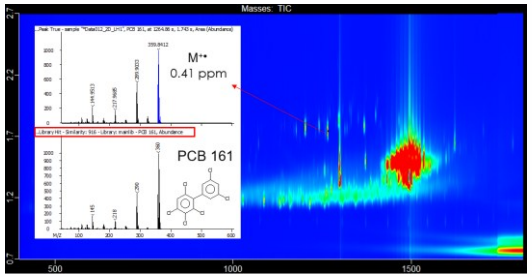

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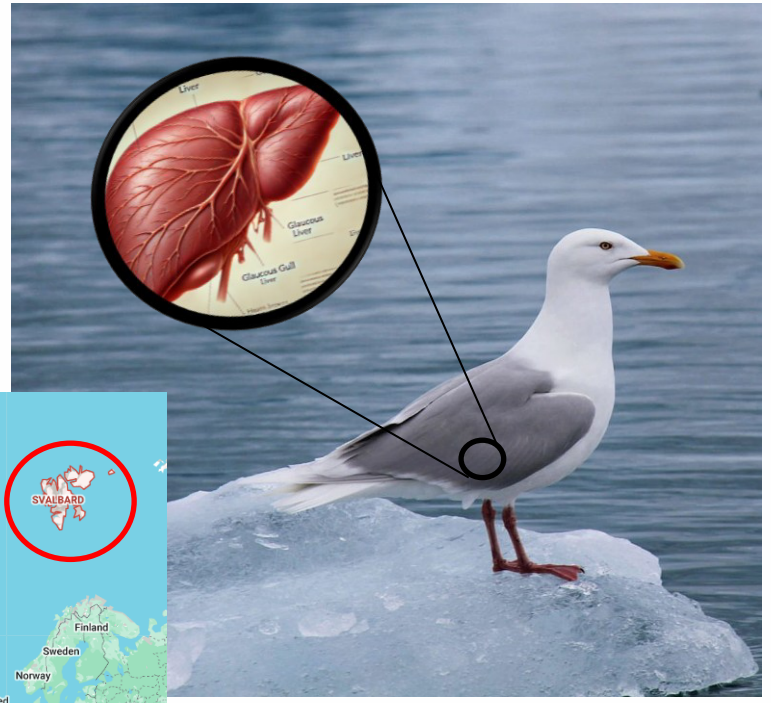

Glaucus gull (Larus hyperboreus) liver extracts inhabiting Svalbard islands

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Sample preparation

Extraction
- 10 g sample
- Homogenization (Dry Na_2SO_4)
- Shaking and ultrasonic bath

Clean-up
- Lipid freezeout
- GPC/SEC chromatography
- Chromatography On Florisil

Fractions
- Non-polar (10% DCM/n-Hex)
- Polar (10% MeOH/DCM)

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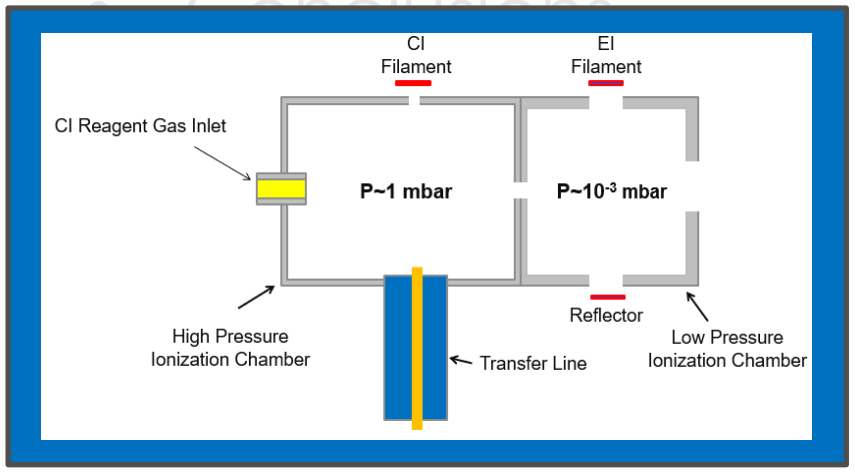

GC×GC & HR-TOFMS parameters

GC	Agilent 8890
Injection	Inj. Temp.: 250 °C; splitless (purge time 120 s)
GC×GC columns:	**^{1}D: Rxi-5SilMS, 30 m x 0.25 mm i.d. x 0.25 µm coating** **^{2}D: Rxi-17SilMS, 0.6 m x 0.25 mm i.d. x 0.25 µm coating**
Carrier Gas	**He** 1.20 mL/min
Oven Program	70 °C (2 min), ramp 10 °C/min to 340 °C, (12 min)
Secondary Oven	+ 5°C
Modulator	+15 °C (relative to the secondary oven temperature)
Modulation Period	Variable (2s, 3.2s and 6s)
Transfer line	330 °C
MS	**LECO Pegasus® HRT+4D**
Ion source	MMS with EI/PCI/ECNI
Ion Source Temp	250 °C (EI); 180°C (ECNI)
Mass Range	40-1000 m/z
Acquisition Rate	**150 spectra/s**

Multiple ionizations, same ion source

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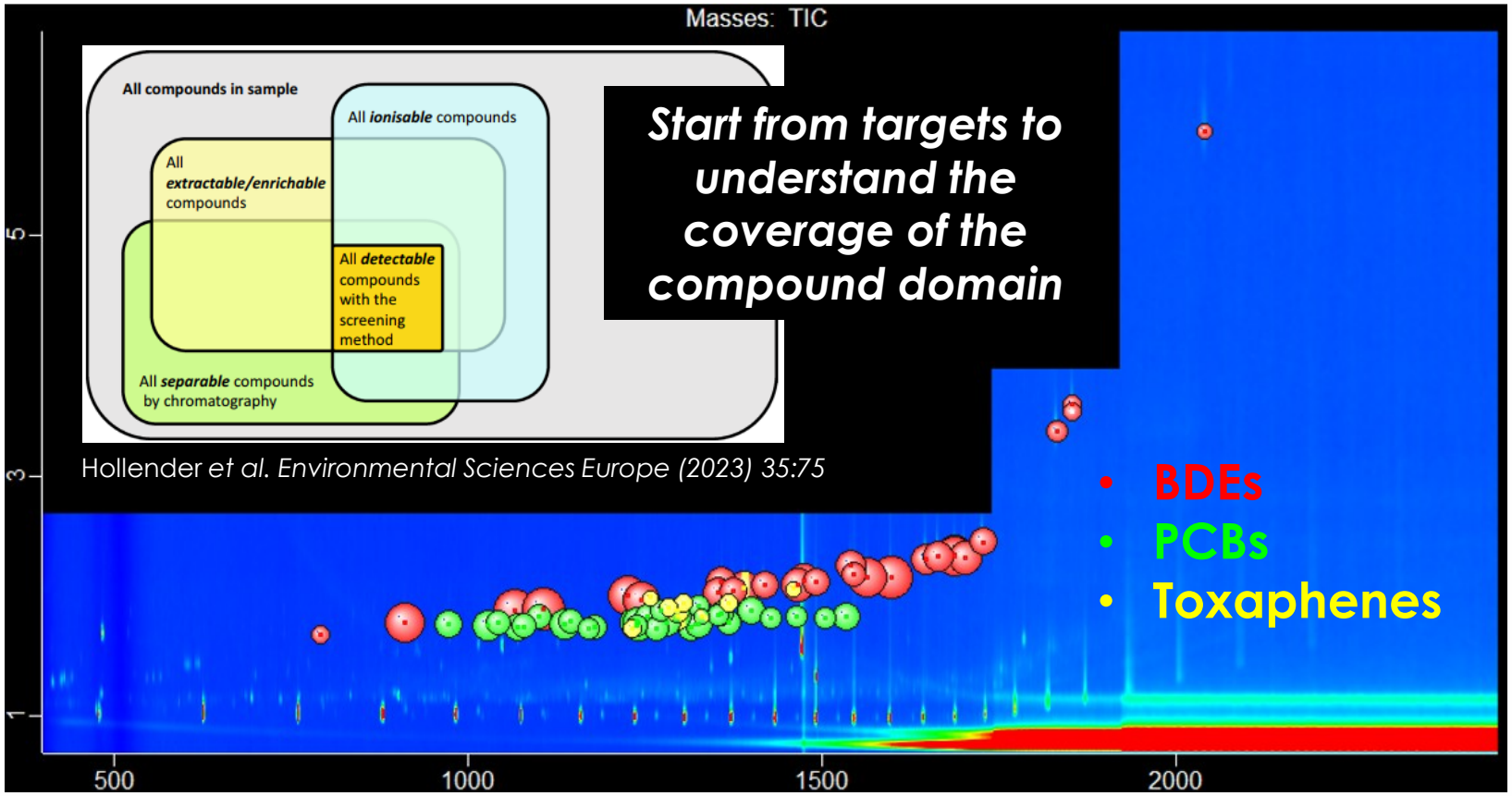
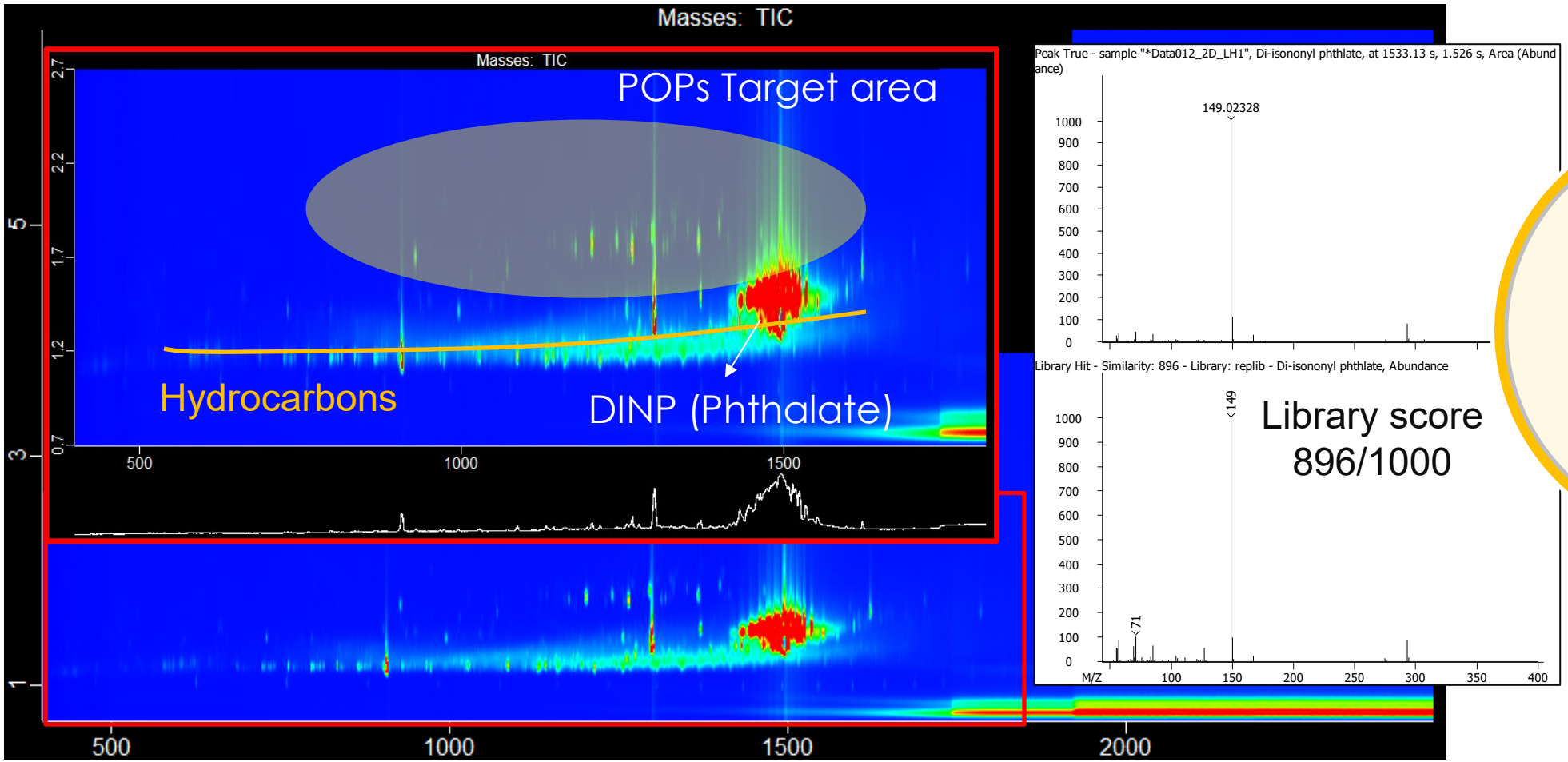
Ionization: EI
Resolution: 25000



Method optimization using BDEs, PCBs and Toxaphenes stds

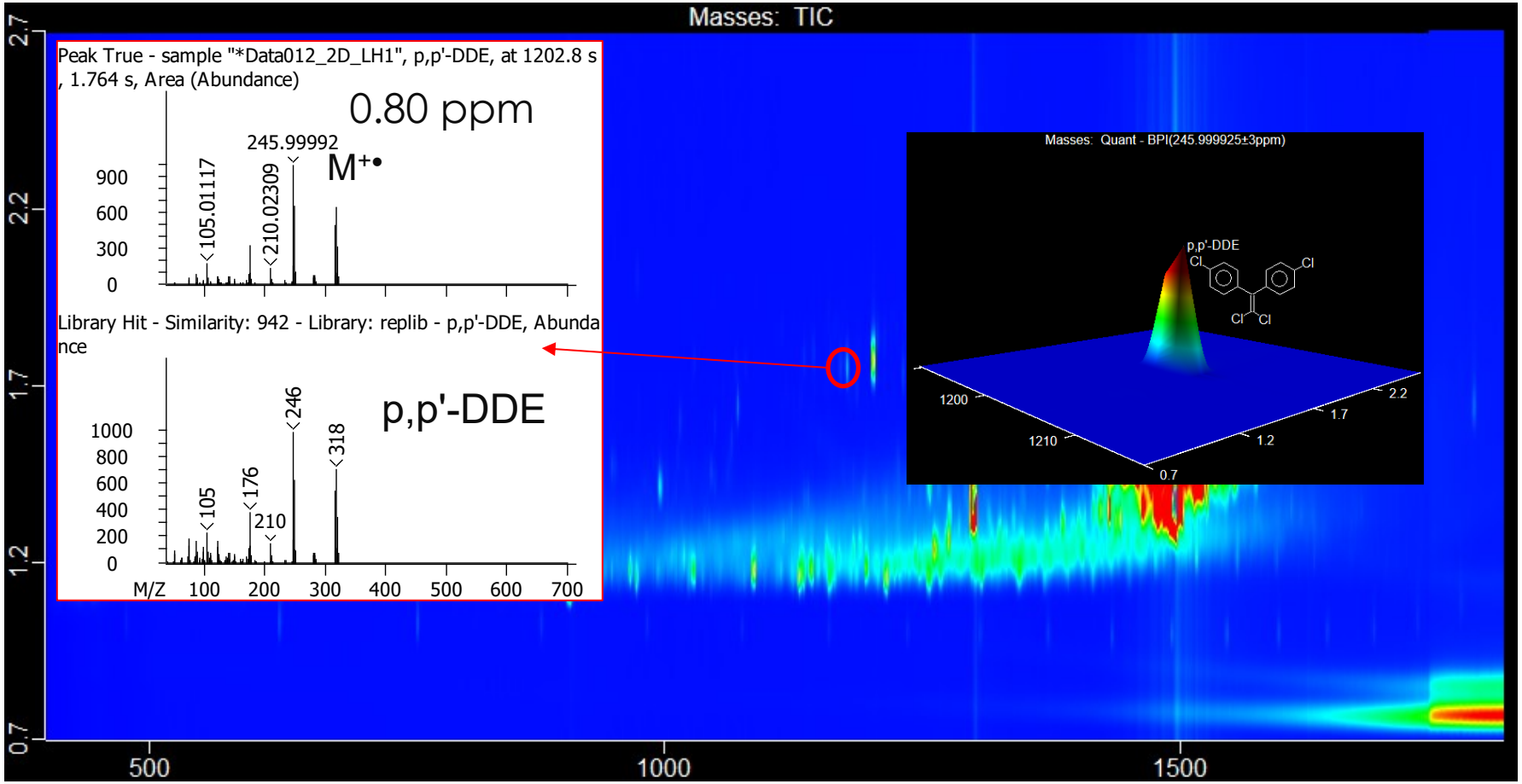
Results



1. Demonstrate the benefits of ***GC×GC*** *for Non-Target/Target screening*

Sample: LH1

Results (NTS)

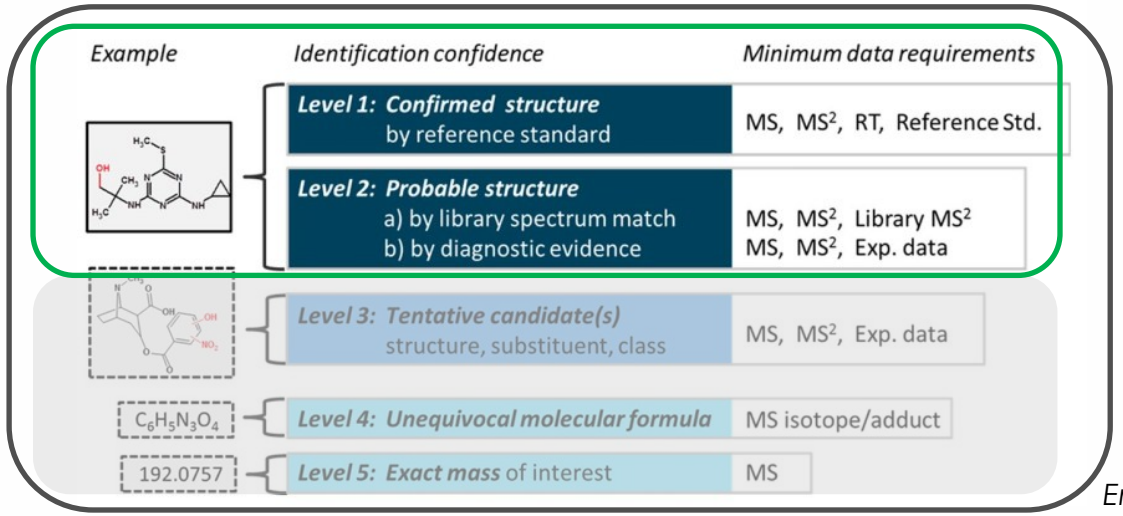


*1. Demonstrate the benefits of **GC×GC** for Non-Target/Target screening*

*2. The role of **HR-TOFMS** and different ionization modes in Non target Analysis*

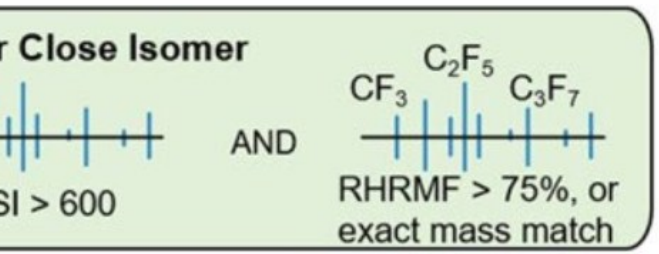
Results

Level of Confidence

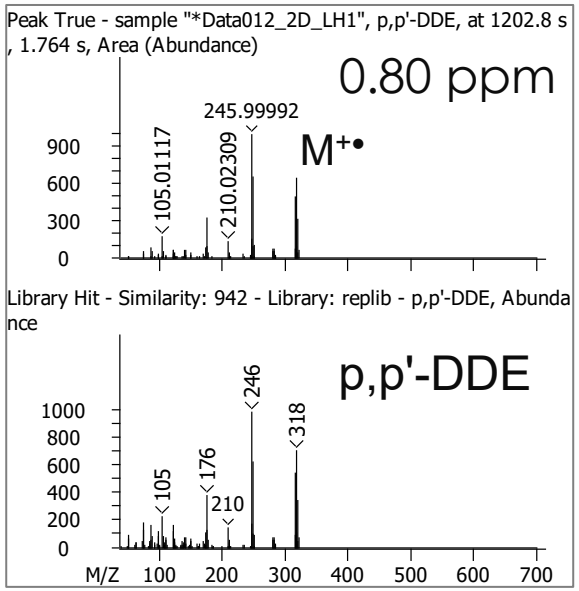


Pure (EI) spectra results in better database matches and thus few initial steps can be neglected (i.e. Levels 3-5)

Environ. Sci. Technol., 48, **2014**, 2097-2098.



Exposome, 25, **2022**, osac007



Δ RI < 50 (**46**) ✓

Reverse similarity search > 600 (**934**) ✓

Exact mass match (MA = **0.80 ppm**) ✓

Results

SSA NTS

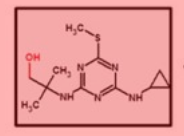
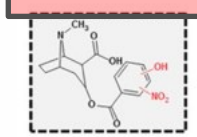
Excerpt list of tentatively identified – EI Data

Name	R.T. (s)	Retention Index	Lib. RI	Similarity	Formula	Quant S/N	Mass Accuracy (ppm)	Expected Ion m/z	Observed Ion m/z
Benzene, pentachloro-	792.392, 1.666	1541.7	1511 ± 9(18)	877	C6HCl5	484	0.48	247.85154	247.85166
Benzene, hexachloro-	928.528, 1.701	1740.6	1707 ± 9(29)	960	C6Cl6	3530	-0.08	281.81257	281.81254
PCB 28+31	1028.63, 1.764	1903.3	1894 ± 5(8)	916	C12H7Cl3	677	-0.51	255.96078	255.96065
PCB 42	1068.67, 1.750	1970	1972 ± 14(6)	906	C12H6Cl4	57	0.04	289.92181	289.92182
PCB 41	1078.68, 1.757	1986.7	1988 ± 15(6)	880	C12H6Cl4	443	-0.03	289.92181	289.9218
Octachlorostyrene	1130.73, 1.645	2078.6	2028 ± 8(2)	809	C8Cl8	120	-0.05	375.75027	375.75025
PCB 58	1134.73, 1.778	2085.7	2082 ± 2(3)	889	C12H6Cl4	986	-0.67	289.92181	289.92162
PCB 56	1144.74, 1.785	2103.8	2094 ± 17(6)	873	C12H6Cl4	1176	0.27	289.92181	289.92189
DDMU	1160.76, 1.799	2134.6		916	C14H9Cl3	522	-1.68	281.97643	281.97596
PCB-87	1162.76, 1.736	2138.5	2162 ± 2(7)	813	C12H5Cl5	118	-0.7	323.88284	323.88261
PCB 82	1176.78, 1.750	2165.4	2184 ± 5(6)	909	C12H5Cl5	3334	-0.03	323.88284	323.88283
Nonachlor	1186.79, 1.687	2184.6		873	C10H5Cl9	634	N/A	439.75825	441.75399
p,p'-DDE	1202.8, 1.764	2215.4	2169 ± 11(32)	942	C14H8Cl4	9951	0.8	315.93746	315.93771
PCB 123	1206.81, 1.841	2223.1	2207 ± 3(3)	835	C12H5Cl5	941	-1.43	323.88284	323.88238
PCB 107	1212.81, 1.834	2234.6	2218 ± 19(2)	852	C12H5Cl5	541	0.57	323.88284	323.88303
1,1'-Biphenyl, 2,3',4,4',5-pentachloro-	1240.84, 1.785	2288.5	2259 ± 18(15)	922	C12H5Cl5	4979	0.28	323.88284	323.88293
m,p'-DDD	1248.85, 1.876	2304.2		793	C14H10Cl4	301	N/A	317.95311	306.9191
PCB 161	1264.86, 1.743	2337.5	2337 ± 1(3)	916	C12H4Cl6	10443	0.41	357.84387	357.84401
PCB-128	1278.88, 1.799	2366.7	2387 ± 15(7)	836	C12H4Cl6	103	-1.32	357.84387	357.8434
2,'3,4',6-Tetrabromodiphenyl ether	1372.97, 2.051	2565.2		848	C12H6Br4O	445	0.14	481.71466	481.71473
Mirex	1403, 1.981	2633.3	2531 ± 8(12)	900	C10Cl12	2422	N/A	539.62568	543.61771
PCB 196	1465.06, 1.827	2781	2553 ± 1(2)	929	C12H2Cl8	3477	-3.33	425.76592	425.76451
PCB 206	1503.1, 1.834	2871.4	2762 ± 24(6)	796	C12HCl9	450	-2.75	459.72695	459.72569
Decachlorobiphenyl	1535.13, 1.827	2952.6	2794 ± 6(6)	783	C12Cl10	327	-3	493.68798	493.6865

Results

ECNI-GC×GC-HRMS in addition to GC×GC EI-HRMS?

Level of Confidence

Example	Identification confidence	Minimum data requirements
	*Level 1: Confirmed structure* by reference standard	MS, MS^2, RT, Reference Std.
	Level 2: Probable structure a) by library spectrum match b) by diagnostic evidence	MS, MS^2, Library MS^2 MS, MS^2, Exp. data
	*Level 3: Tentative candidate(s)* structure, substituent, class	MS, MS^2, Exp. data
$C_6H_5N_3O_4$	*Level 4: Unequivocal molecular formula*	MS isotope/adduct
192.0757	*Level 5: Exact mass* of interest	MS

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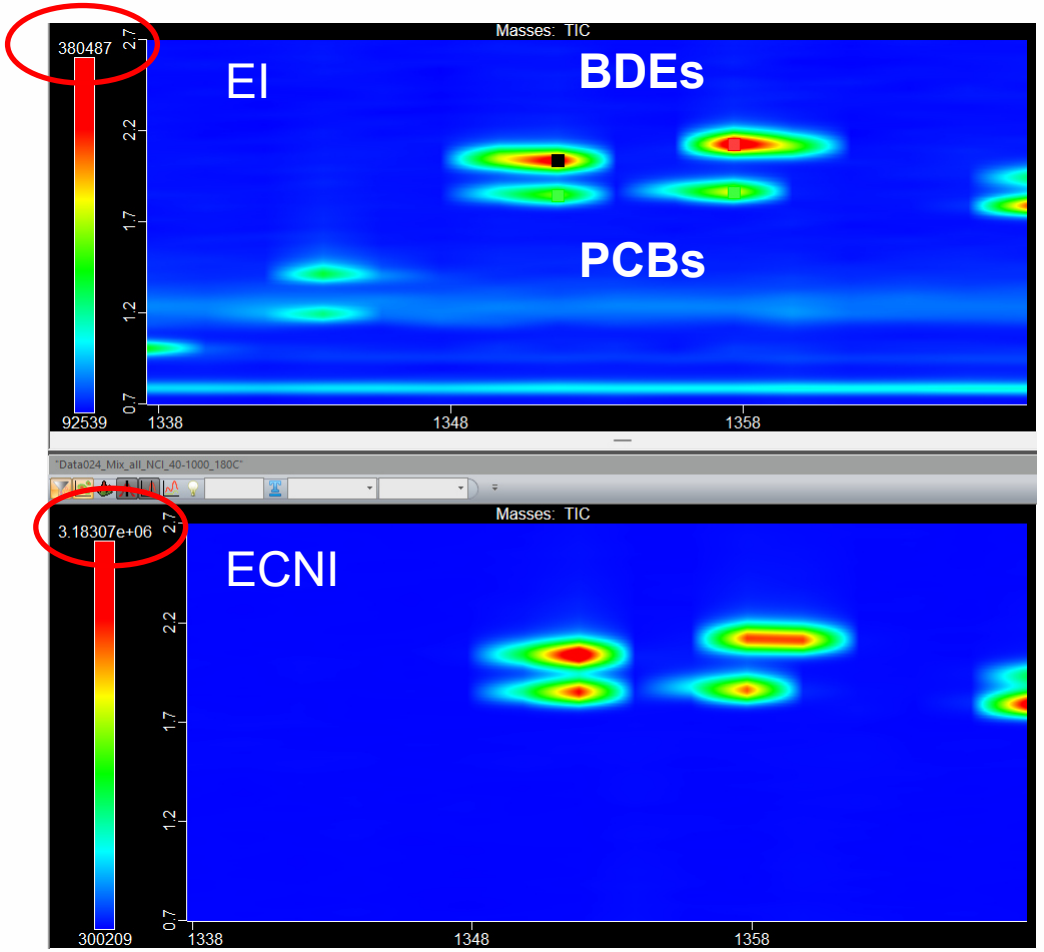
- Low library score
- No molecular ion
- Uncertain identification

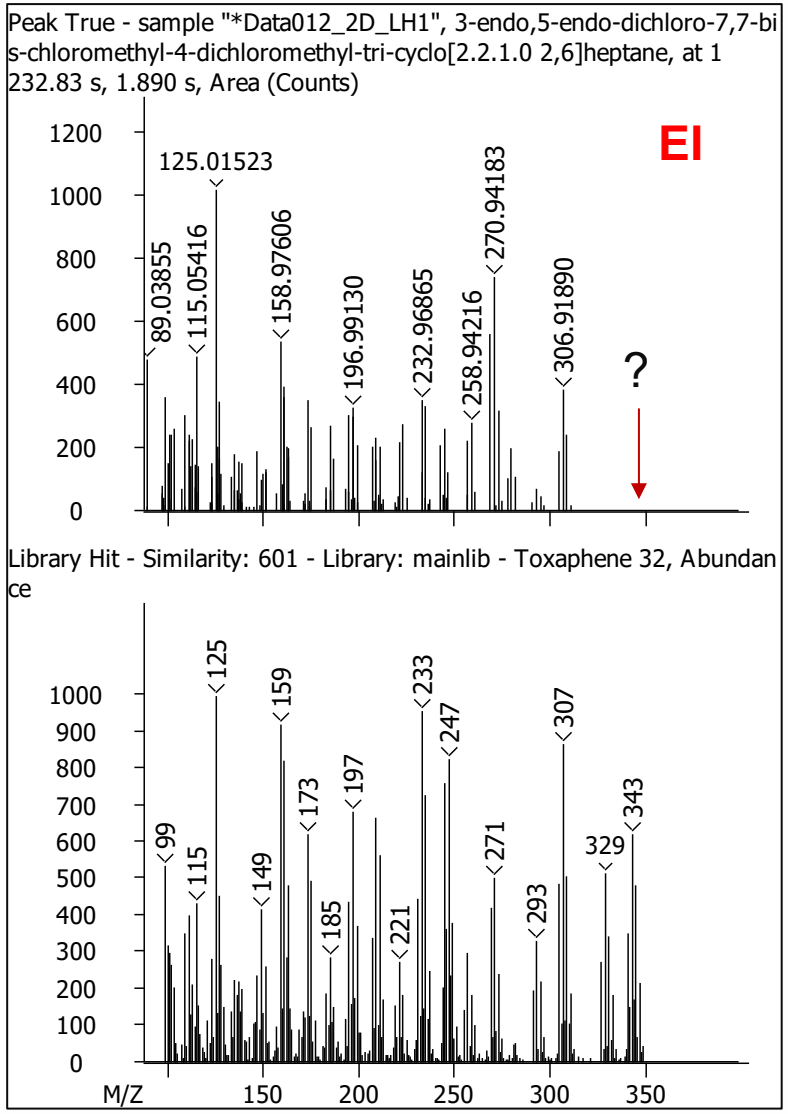


EI

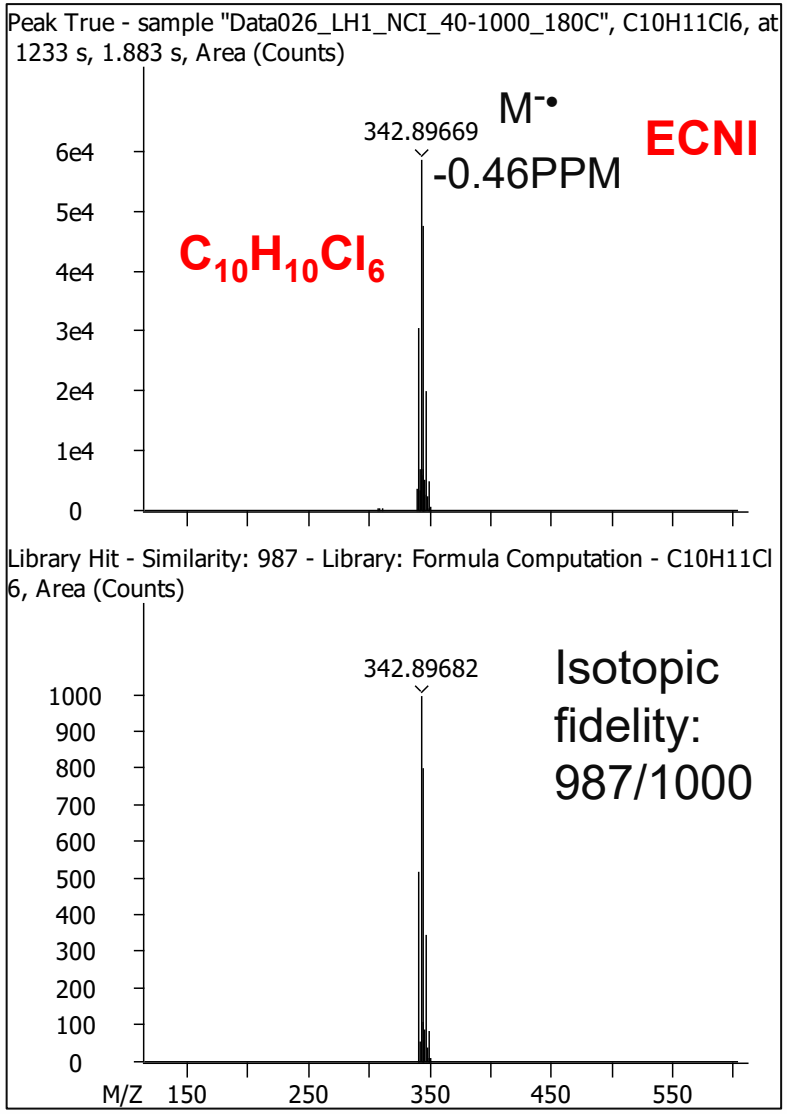
Increase Selectivity/Sensitivity

ECNI

Identification via ECNI



Library spectrum



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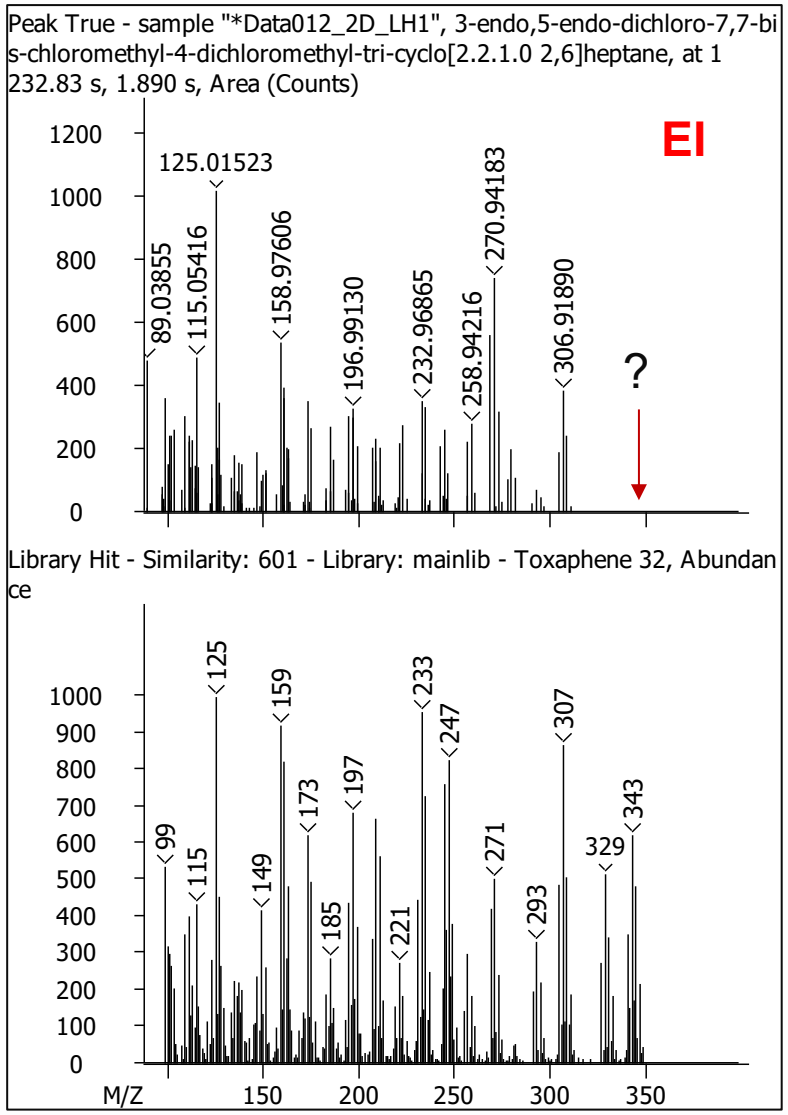

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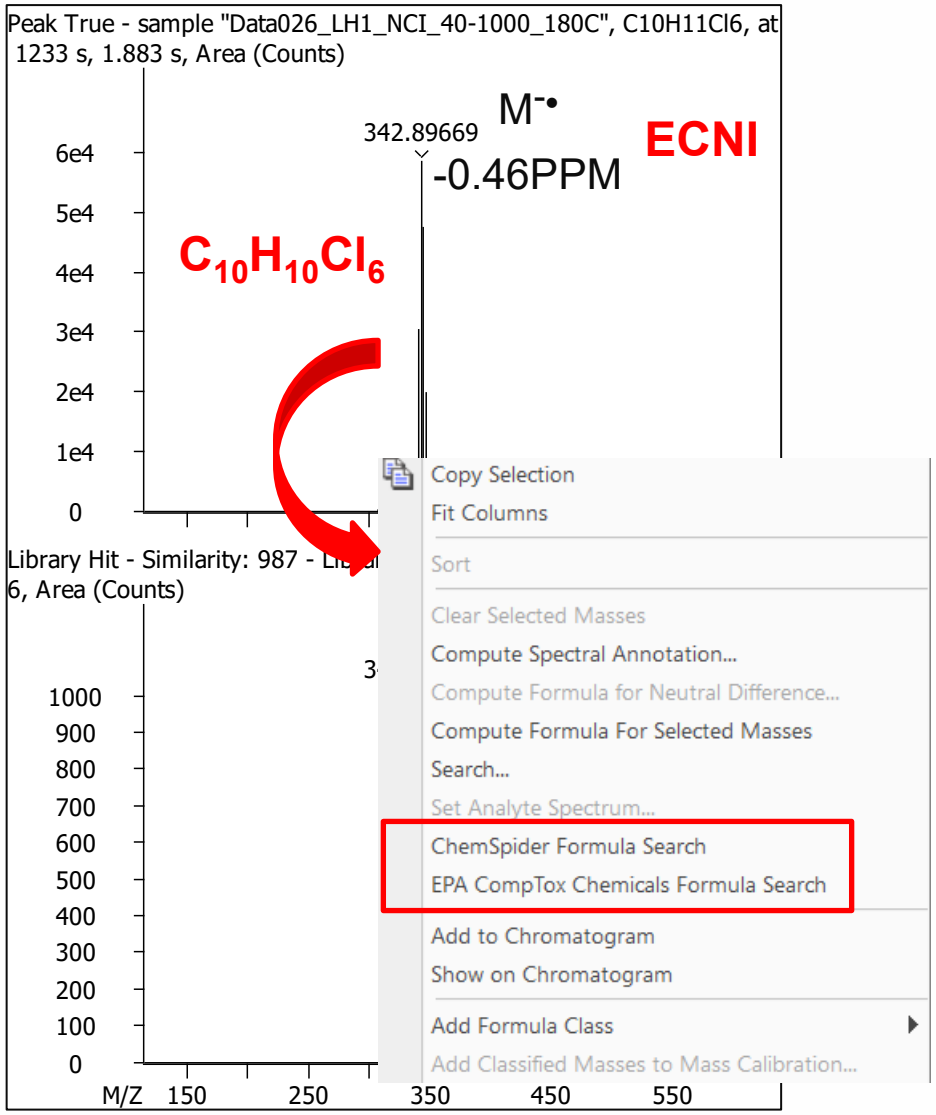

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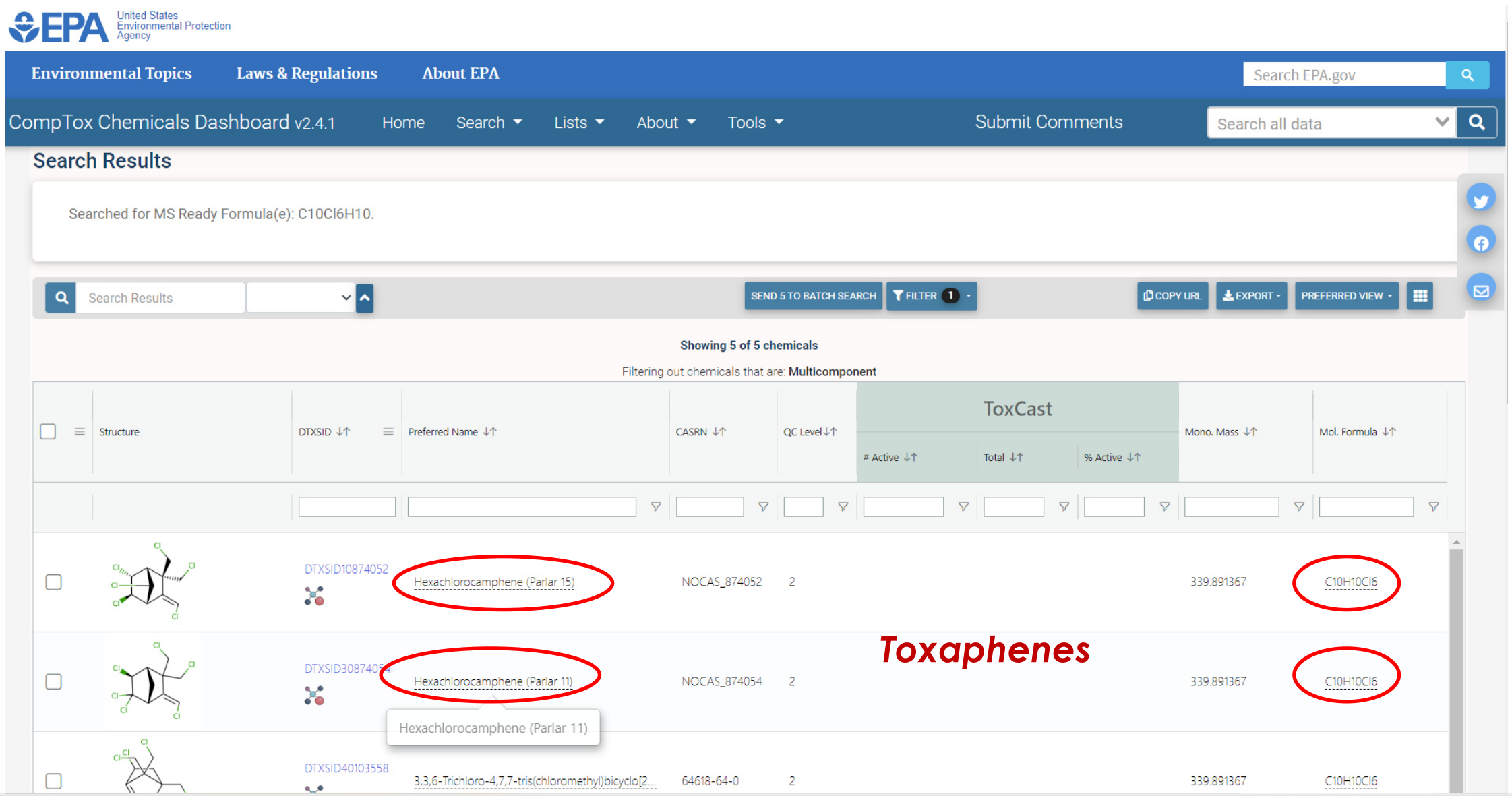
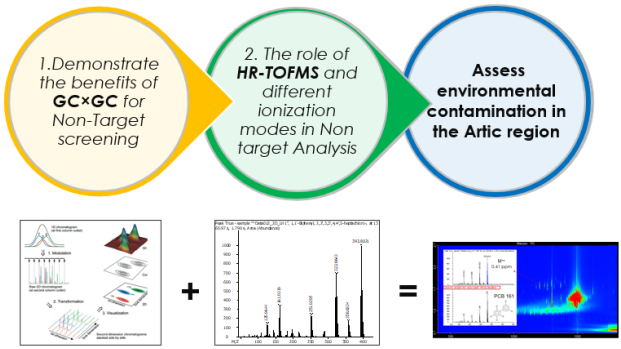


Conclusions

- **GC×GC**-HRTOFMS is a powerful "discovery" tool thanks to the improved separation capabilities and structured contour plots. Patterns of elution help the identification process

- GC×GC**-HRTOFMS** helps to complete the "story" thanks to the accurate mass information and complementarity of EI / ECNI ionization modes.

- The information gained from these samples will help to understand better the environmental exposure and potential threats to these avian species and their habitats in this sensitive Arctic region.



Beer Analytical Tasting Event

6 pm "Salle des Professeurs"