ANALYSIS OF DIOXINS, FURANS AND POLYCHLORINATED BIPHENYLS IN SEDIMENTS AND FISH USING NOVEL 7250 HIGH-RESOLUTION GC/Q-TOF

OVERVIEW
- The aim was to demonstrate how **high-resolution GC/Q-TOF instruments** can be used for **flexible analysis of dioxin-like compounds**
- Full spectra EI data was collected using the novel Agilent 7250 GC/Q-TOF and was queried using **target, suspect and non-target analysis workflows**
- We demonstrate **excellent accuracy in dioxin and dioxin-like PCB analyses**
- We illustrate how GC/Q-TOF instruments allow **screening for known dioxin-like compounds** and **identification of unknown dioxin-like compounds**

Introduction

- Dioxin-like compounds bind to the Ah receptor and produces toxic effects at very low levels[1]

- Strong Ah ligands are all planar aromatic compounds and most are halogenated

- The total dioxin-like toxicity can be expressed as dioxin toxic equivalents (TEQs)[2]

- Modern GC time-of-flight MS instruments are very sensitive and provide full EI spectra

- GC/Q-TOF instruments can be used for target analysis of dioxins and dioxin-like PCBs, and for suspect and non-target screening of dioxin-like compounds

Methods

Samples and clean-up

- Baltic Sea sediment and fish: in-house reference materials (RMs)

- Sediment was Soxhlet extracted with toluene

- Fish was column extracted with acetone:hexane and hexane:ether

- Bulk matrix was removed by H_2SO_4 treatment

- Planar compounds were isolated through carbon column clean-up

GC-QTOF MS

- GC high-resolution EI-MS analysis was performed on an Agilent 7250 GC/Q-TOF

- Target compounds were detected by MassHunter (MH) Find-by-Fragments workflow

- MH Quantitative Analysis was used for quantification

- MH Qualitative Analysis was used for suspect screening of dioxin-like compounds

- MH Unknown Analysis was used for non-target screening of dioxin-like compounds

Peter Haglund[1], Sofia Nieto[2], Nathan Eno[2]

1 Umeå University, Umeå, Sweden; 2 Agilent Technologies, Inc., Santa Clara, CA, USA.

Results – Target Analysis

Table 1: Comparison of GC/Q-TOF and GC-magnetic sector high-resolution MS data (pg/g)

Congener	TEF*	Sediment			Salmon		
		QTOF HRMS	Sector HRMS	RM Average	QTOF-HRMS	Sector-HRMS	RM Average
PCB-77	0.0001	32	37	36	1125	900	910
PCB-81	0.0003	3.5	1.8	1.8	23	23	26
PCB-126	0.1	8.8	8.0	7.3	464	410	430
PCB-169	0.03	3.9	1.8	1.6	53	53	58
2,3,7,8 -TCDD	1	1.8	1.5	1.5	2.3	2.6	2.7
12378 -PeCDD	1	3.2	3.2	2.8	4.7	4.4	4.6
123478 -HxCDD	0.1	6.4	1.8	2.1	0.4	0.3	0.3
123678 -HxCDD	0.1	14	11	11	3.0	1.7	1.9
123789 -HxCDD	0.1	8.2	7.0	6.8	0.2	0.1	0.2
HpCDD	0.01	40	34	36	0.7	0.3	0.3
OCDD	0.0003	137	100	113	1.9	0.9	1.2
2378 -TCDF	0.1	13	14	17	26	23	23
12378 -PeCDF	0.03	4.7	4.1	4.2	4.2	5.4	5.0
23478 -PeCDF	0.3	11	10	9.4	29	26	25
123478 -HxCDF	0.1	7.0	7.1	9.1	1.3	0.9	0.9
123678 -HxCDF	0.1	10	5.1	4.5	2.7	1.2	1.2
234678 -HxCDF	0.1	8.5	6.1	6.1	1.5	1.0	0.9
123789 -HxCDF	0.1	3.7	1.9	2.3	ND	0.2	0.2
1234678 -HpCDF	0.01	95	76	77	0.2	0.3	0.3
1234789 -HpCDF	0.01	8.0	3.1	3.4	ND	0.1	0.1
OCDF	0.0003	130	94	105	1.6	0.2	0.3
TEQ		18	15	15	67	60	63

* TEF: World Health Organization (WHO) Toxic Equivalency Factor.

- Good agreement of planar PCB and polychlorinated dibenzo-p-dioxin and dibenzofuran (PCDD/F) concentrations from GC-QTOF-MS and GC-magnetic sector-MS (Table 1)

- The important tetra/penta-CDD/Fs, PCB-126, and TEQ are within ±25% of the reference values

- The deviation between QTOF-MS and Sector-MS data depends on the signal quality (S/N ratio) and is less than ±40% for all compounds with a S/N greater than 10

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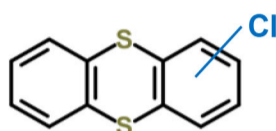
Results: Suspect screening

Suspects
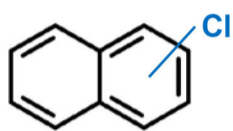
Chlorinated napthalene (PCN)
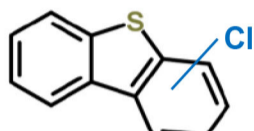
Chlorinated dibenzothiophene (PCDT)

Chlorinated Thinanthrene (PCTA)

- PCTAs were not detected

- PCDT were found in sediment at 10% of the PCDD/F levels

- **PCNs were most abundant** (**Figure 1**)

- PCN and PCDF levels were similar in sediment

- PCN levels were 100-fold higher than PCDD/F levels in salmon

- Metabolically stable PeCNs and HxCNs (wo. vicinal hydrogens) biomagnify in fish

Figure 1. PCN composition
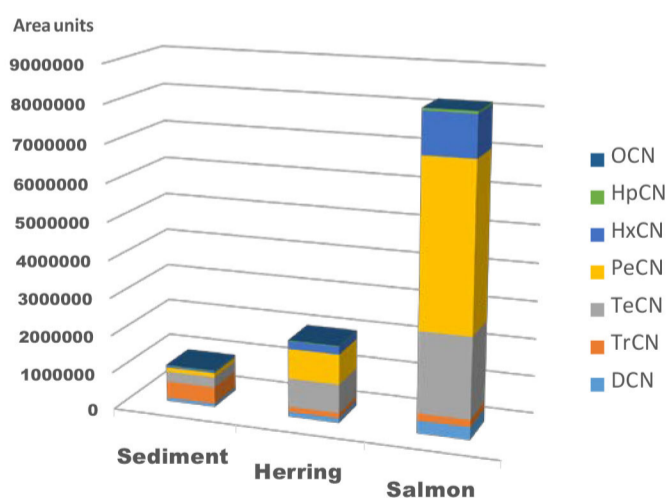
Sediment: Non-target screening

- Polycyclic aromatic compounds (PACs), incl. PAHs, dominated the dioxin fraction

- **Halogenated PAHs** was also found (**Figure 2**)

- Halo-PAHs were dominated by lower halogenated congeners (**Figure 3**)

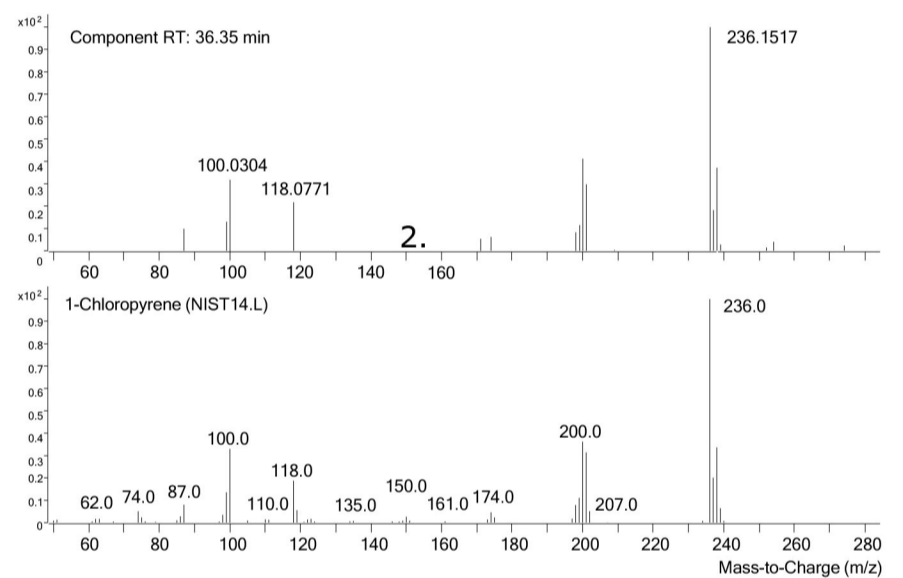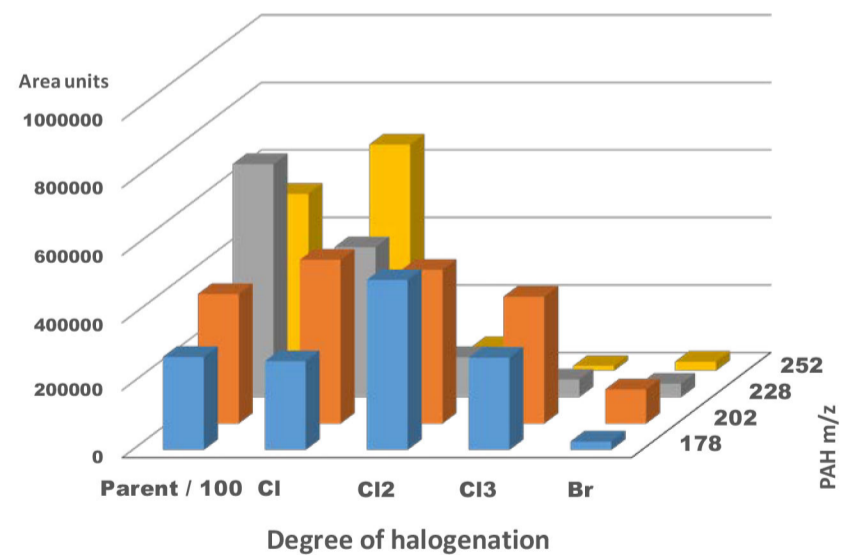**Figure 2.** Tentative identification of chloropyrene

Figure 3. PAHs and halo-PAHs in sediment

References

1. http://www.euro.who.int/__data/assets/pdf_file/0017/123065/AQG2ndEd_5_11PCDDPCDF.pdf?ua=1

2. https://www.epa.gov/toxics-release-inventory-tri-program/dioxin-and-dioxin-compounds-toxic-equivalency-information

Sediment: Non-target screening

- An abundant brominated unknown with formula $C_{13}H_7NBr_4$ was found in sediment (**Figure 4**)

- A Chemspider search returned on candidate: **1,3,6,8-Tetrabromo-9-methyl-carbazole**

- $C_{13}H_7NBr_4$ unknown can be a metabolite of the natural product 1,3,6,8-Tetrabromocarbazole [1], which was also detected (**Figure 5**)

- The isotope clustering and fragmentation is supporting the proposed structure
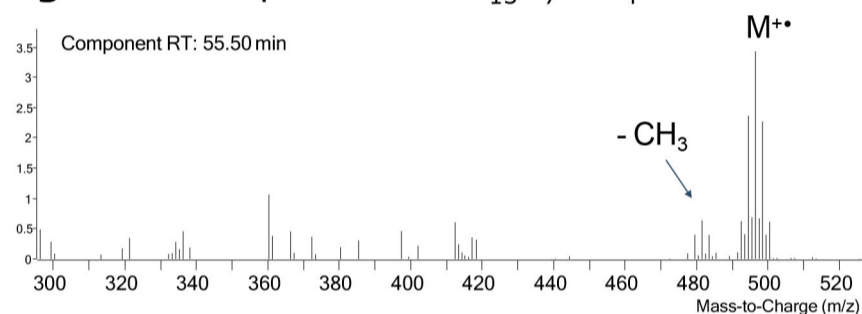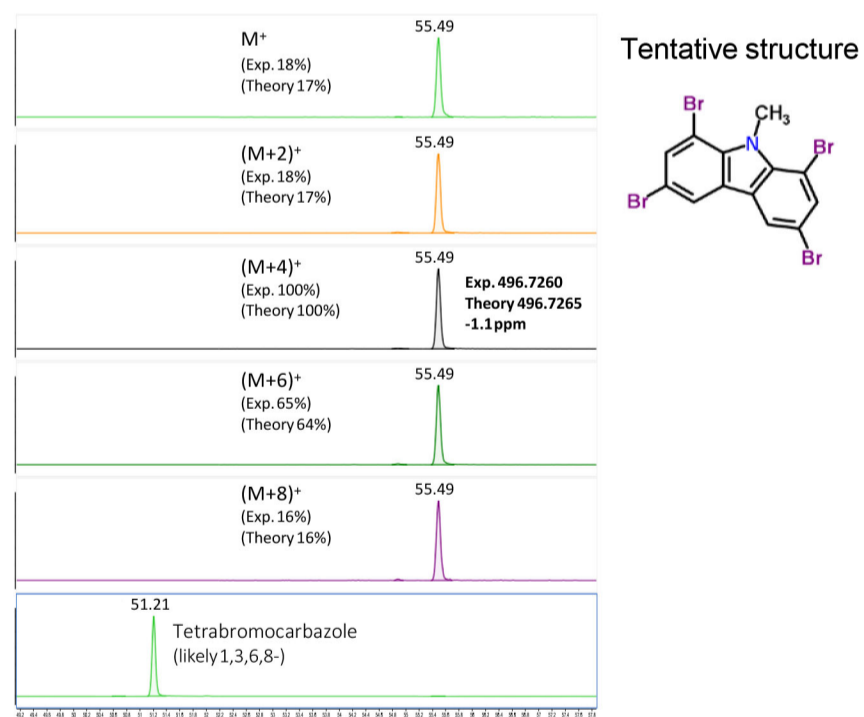
Figure 4. EI spectrum of $C_{13}H_7NBr_4$

Component RT: 55.50 min

$M^{+\bullet}$

$- CH_3$

Mass-to-Charge (m/z)

Figure 5. Isotope fidelity of $C_{13}H_7NBr_4$

M^+
(Exp. 18%)
(Theory 17%)
55.49

$(M+2)^+$
(Exp. 18%)
(Theory 17%)
55.49

$(M+4)^+$
(Exp. 100%)
(Theory 100%)
55.49
Exp. 496.7260
Theory 496.7265
-1.1ppm

$(M+6)^+$
(Exp. 65%)
(Theory 64%)
55.49

$(M+8)^+$
(Exp. 16%)
(Theory 16%)
55.49

Tetrabromocarbazole
(likely 1,3,6,8-)
51.21

Tentative structure

[1] Identification of Brominated Carbazoles in Sediment Cores from Lake Michigan. *Environmental Science and Technology* **39**:9446-9451.

Summary: Sediment contaminants

- PAHs dominated the dioxin fraction (**Figure 6**)

- Halo-PAHs and brominated carbazoles and methyl carbazoles (BR-CZ/MCZ) were present at ca 100-fold lower levels

- PCNs, PCDFa and PCDDs were at comparble levels, whilst PCDTs were 10-fold lower

- Tetrahalogentated congeners dominated the bi-tricyclic planar compound groups (**Figure 7**)

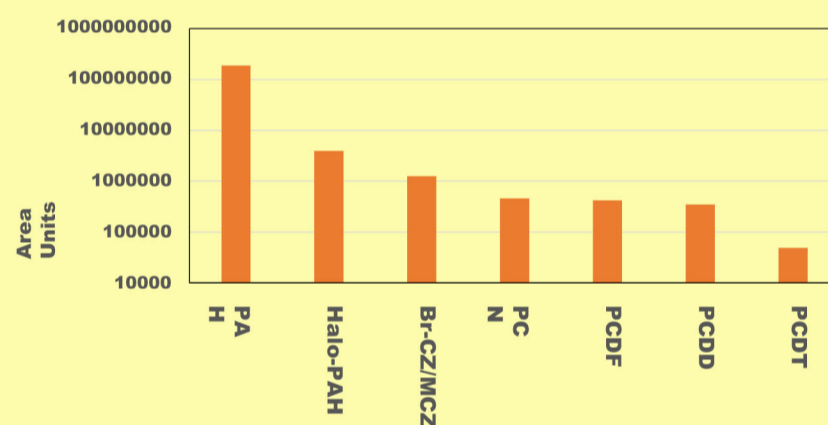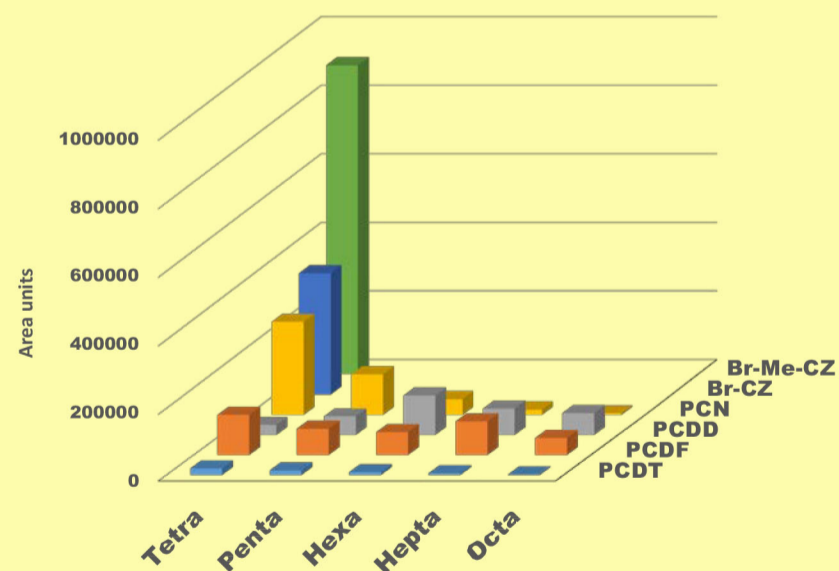**Figure 6.** Concentrations in sediment

Figure 7. Congener distribution in sediment

Conclusion

The new GC-QTOF system generates PCDD/F and planar-PCB concentrations comparable to those of the Golden Standard: Magnetic sector HRMS

Full spectrum data is obtained in the same run, which can be used for suspect and non-target screening of other dioxin-like compounds