Recent Advances in the Analysis of Pyrethroid Insecticides in Surface Water and Sediments

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Outline

- Aquatic Toxicity of Pyrethroids
- GC/QQQ with Chemical Ionization and Backflushing
- Results
- Conclusions

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Why go to Lower Detection Limits?

- There is a direct (toxic) effect to aquatic and terrestrial organisms from pyrethroid exposure and an indirect effect because of the threat to their food supply.

- Synthetic pyrethroids are known endocrine disruptors and many may be carcinogenic (USEPA).

- Synthetic pyrethroids are extremely toxic to aquatic organisms with LC_{50} values < 1 ppb.

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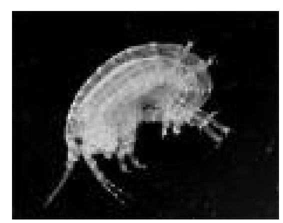
Toxicity in Water and Sediment

Pesticide	Water		Sediment	
	LC_{50} (ng/L)	Organism	LC_{50} (µg/kg)	Organism
Bifenthrin	70	*Hyalella azteca*[1]	4-10	*Hyalella azteca*[2]
Cyfluthrin	140	*Ceriodaphnia dubia*[1]	4-10	*Hyalella azteca*[2]
Cypermethrin	1.5	*Hyalella azteca*[3]	3-6	*Hyalella azteca*[3]
Esfenvalerate	70	*Ceriodaphnia lacustris*[1]	4-10	*Hyalella azteca*[2]
λ-Cyhalothrin	4	*Hyalella azteca*[4]	4-10	*Hyalella azteca*[2]
Permethrin	30	*Hyalella azteca*[1]	4-10	*Hyalella azteca*[2]

1 From previous slide
2 Amwag et al., 2005, *Environ. Toxicol. Chem.*, 24, 966-972.
3 Maund et al., 2002, *Environ. Toxicol. Chem.*, 21, 9-15.
4 Maund et al, 1998, *Pestic. Sci.*, 54, 408-417.



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Detection Limits Needed

Optimal MDL use LC_{50}/10

- Water: ~ **0.2** ng/L
- Sediment: ~ **0.3** ng/g

MDL equal to LC_{50}

- Water: ~ **2** ng/L
- Sediment: ~ **3** ng/g

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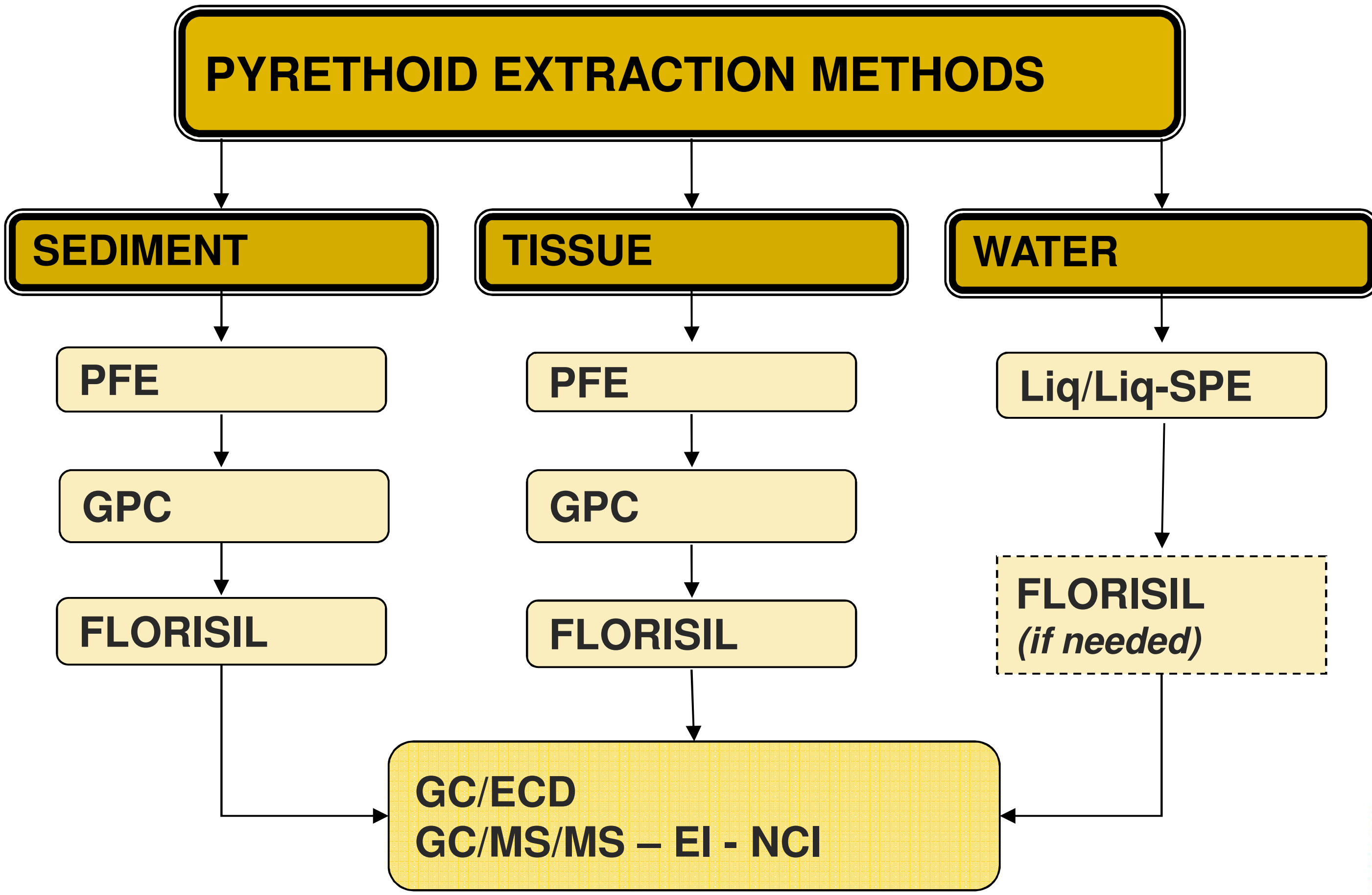
Improving MDLs

- Larger sample and/or injection volumes
- Use of MS/MS – lowers background noise
- Negative Chemical Ionization (nCI) – effective for pyrethroids with Cl, F, or Br

DFG Sample Preparation/Analysis



PFE: Pressurized Fluid Extraction
GPC: Gel Permeation Chromatography

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Analytical Instrument Comparison for Pyrethroids

Instrument: GC-ECD

Advantage	Disadvantage
very sensitive (1-5 pg on column)	dual column required for confirmation, therefore dual data processing
specific for halogenated compounds	rely on retention times for confirmation
excellent screening tool	requires extensive clean-up (sediment and tissue)
affordable	extensive matrix interference
easy to operate	cannot distinguish between deltamethrin and tralomethrin

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Instrument: GC-MS Ion trap in MS-MS mode

Advantage	Disadvantage
sensitivity comparable with ECD (2-10 pg)	narrow linearity range
MS spectra confirmation	trap clean-up needed for tissue
no matrix interference	requires experienced MS chemist
less data handling	cannot distinguish between deltamethrin and tralomethrin
short run time	

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Instrument: LC-MS-MS

Advantage	Disadvantage
sensitivity comparable with GC-MS-ion trap	not as sensitive as GC-MS-QqQ due to polarity of compounds
best result will be obtained by APCI	requires specially trained MS chemist
distinguishes between deltamethrin and tralomethrin	very expensive
excellent for thermo labile compounds	
minimum sample clean-up required	
excellent linearity	
very promising for chiral separation	
green chemistry	

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Instrument: GC-MS Triple-quadrupole (QqQ)

Advantage	Disadvantage
extremely sensitive (0.1-2.0 pg on column)	maintenance needed frequently
excellent for trace level in sediment and tissue	very experienced MS chemist needed
detects halogenated and non-halogenated pyrethroids	expensive
best analytical tool for pyrethroids	cannot distinguish between deltamethrin and tralomethrin

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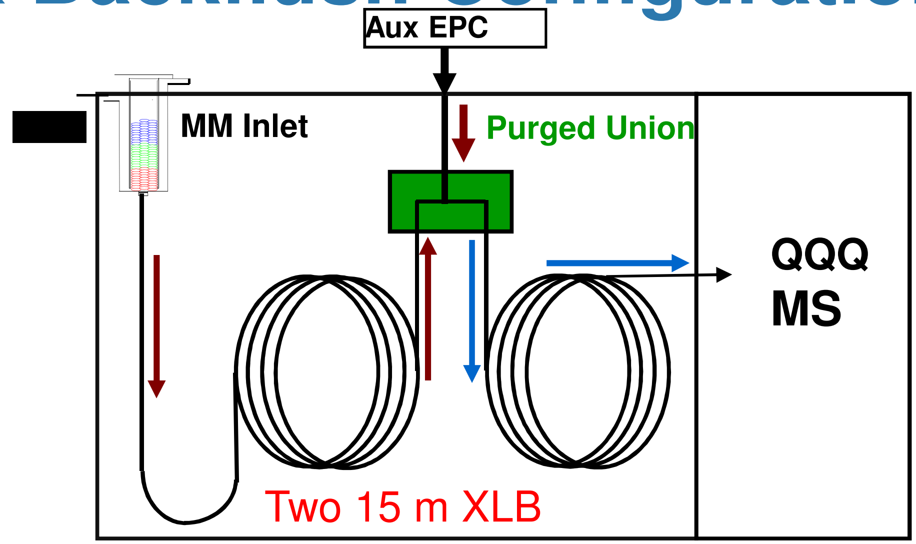
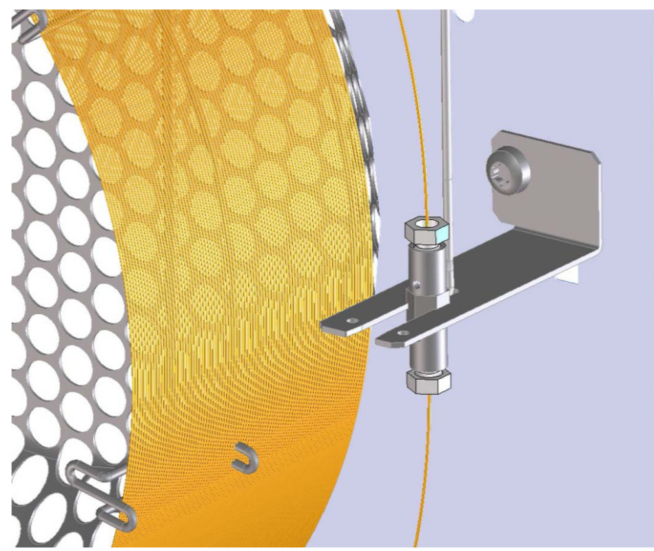
Instrumentation & Backflush Configuration



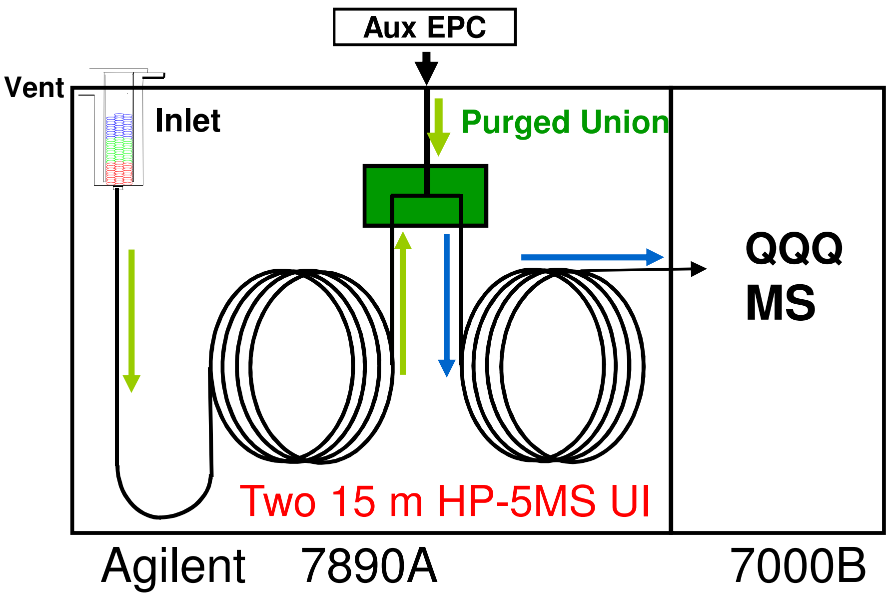
Agilent 7890A/7000B GC/QQQ
With Chemical Ionization



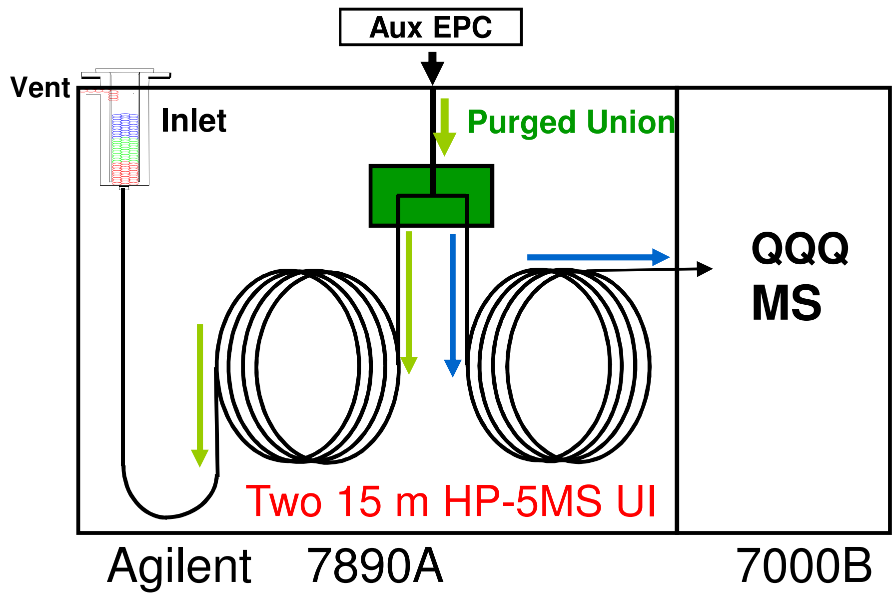
Purged Ultimate Union

Mid-column Backflush

Injection & analysis



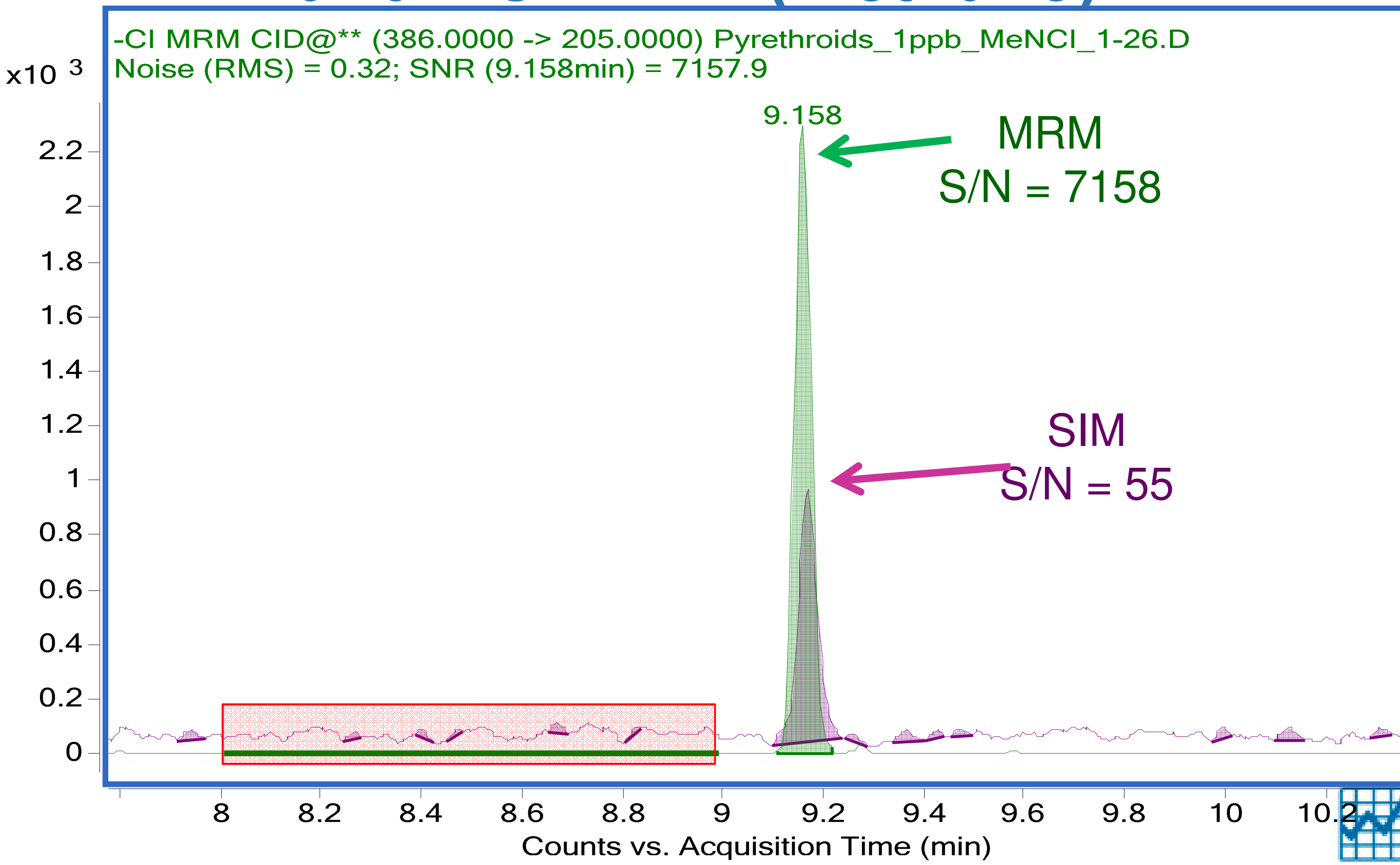
During Backflush



Begin backflushing after last analyte passes purged union
or during post run

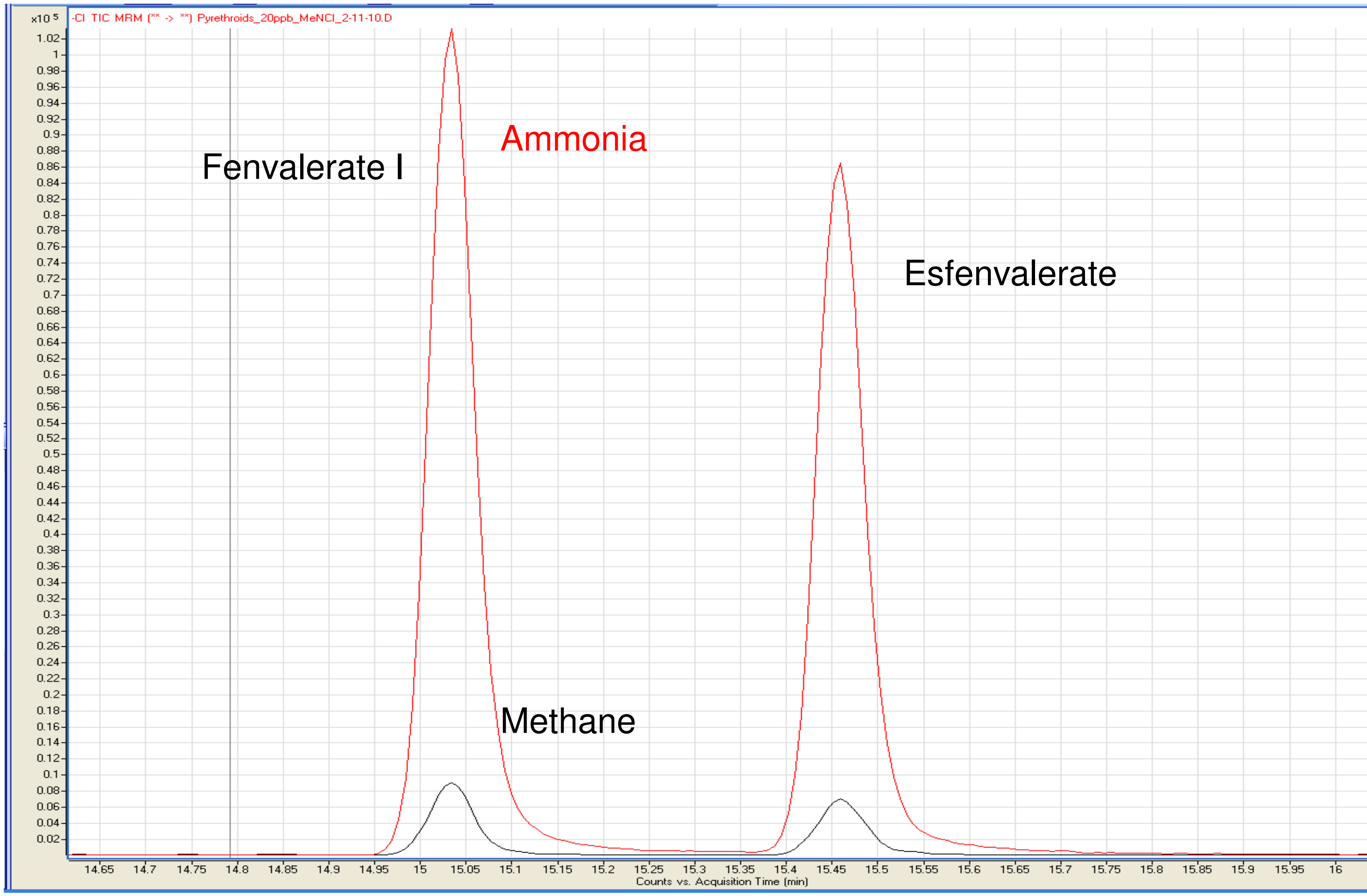
Ambient Monitoring Program

Bifenthrin, 1 ppb Standard: NCI-SIM and NCI-MRM (methane)



MRM transition: 386→205 (green)
SIM ion: 386 (purple)

Comparing Methane and Ammonia Reagent Gases for NCI GC/MS/MS Analysis of Pyrethroids



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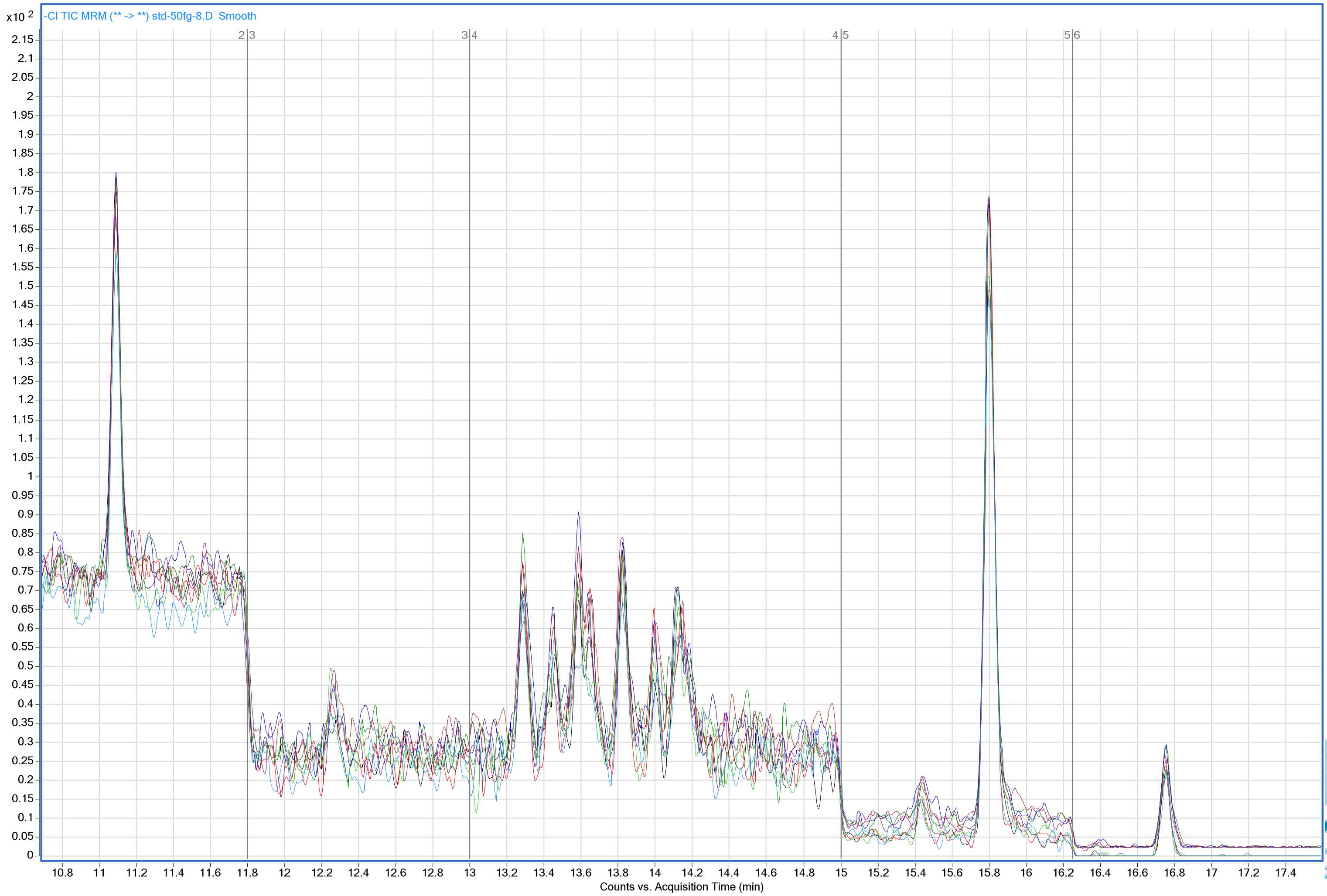
Pyrethroids-50fg (n=8)-NCI



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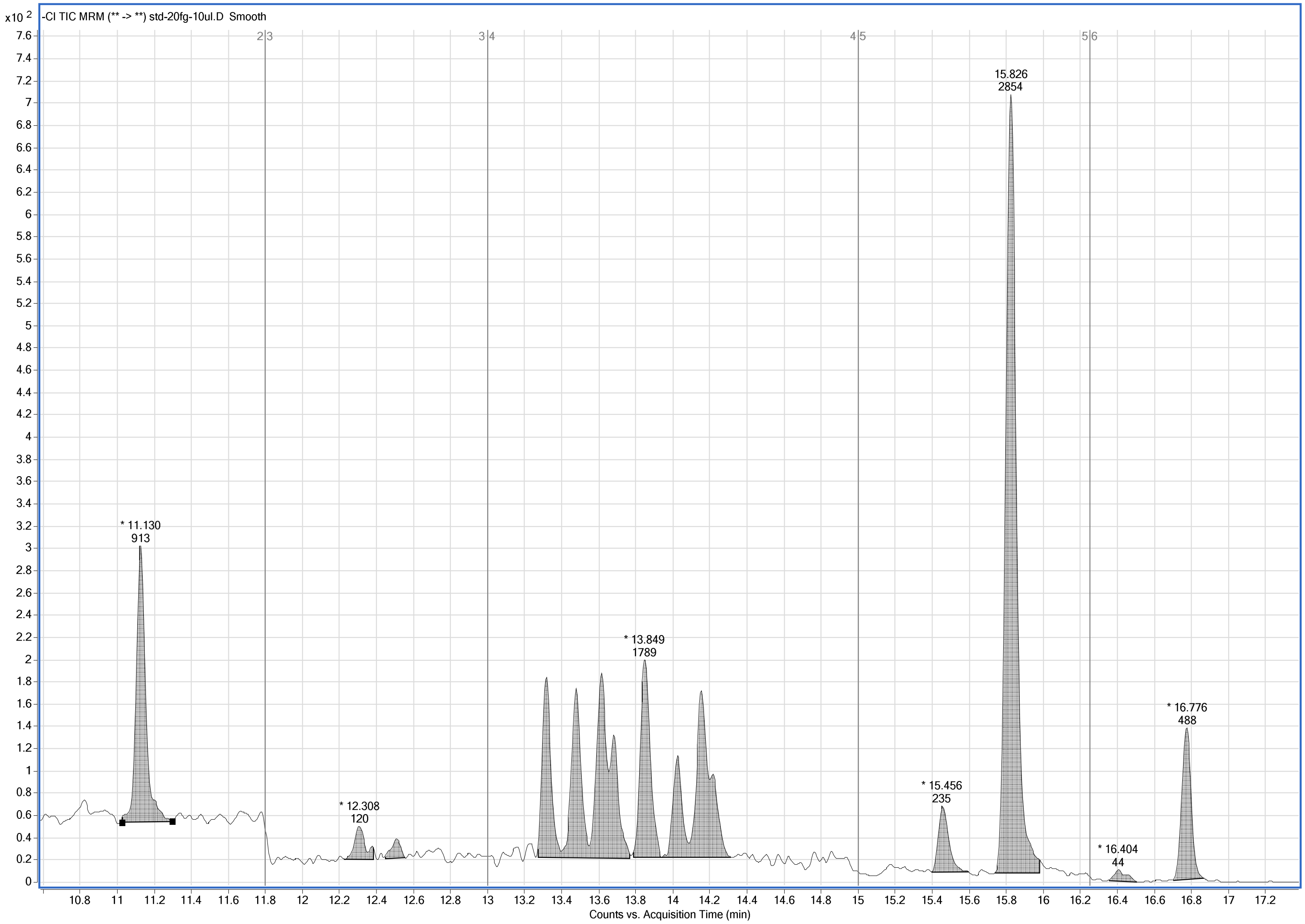
Pyrethroids-20fg-NCI-large volume injection



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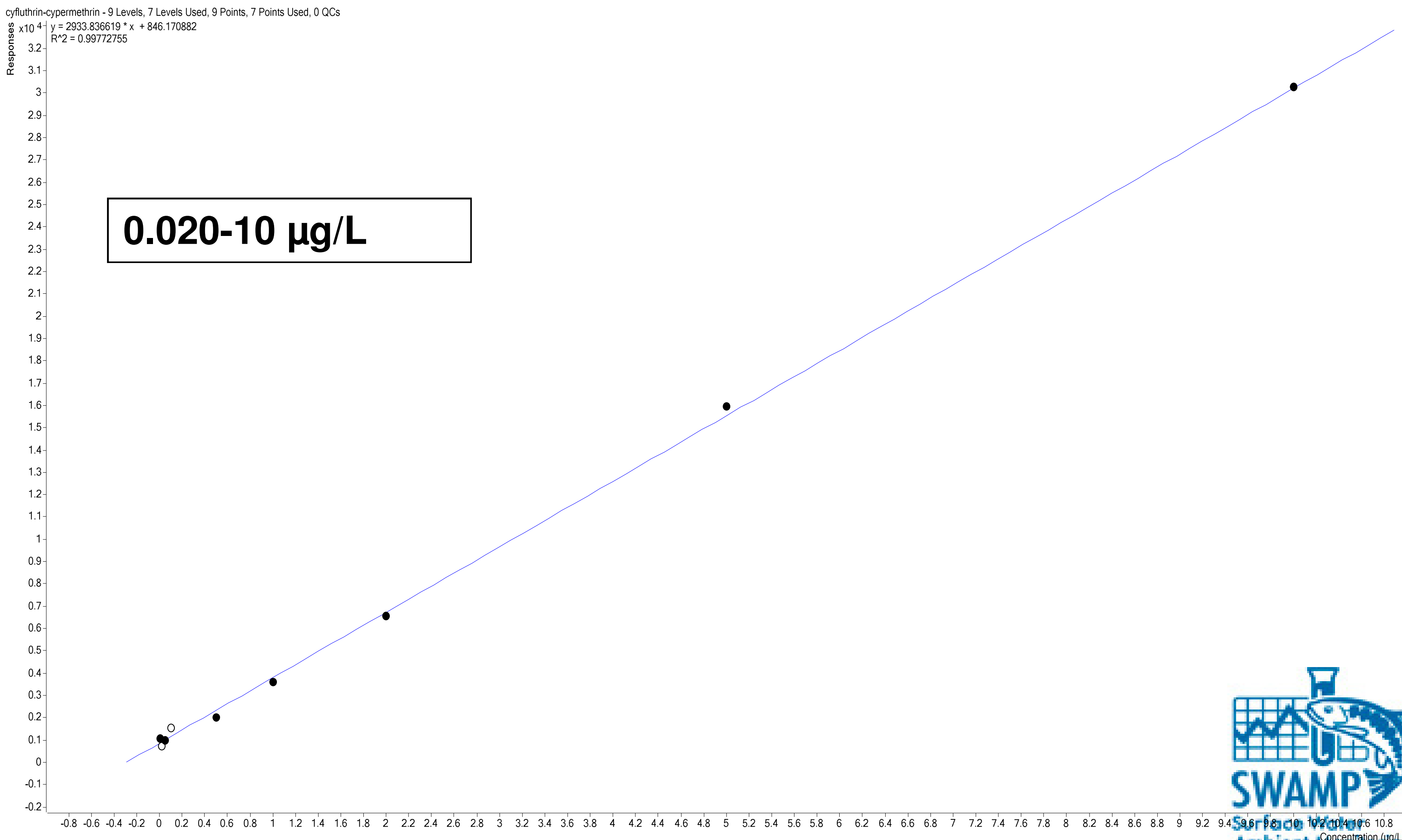
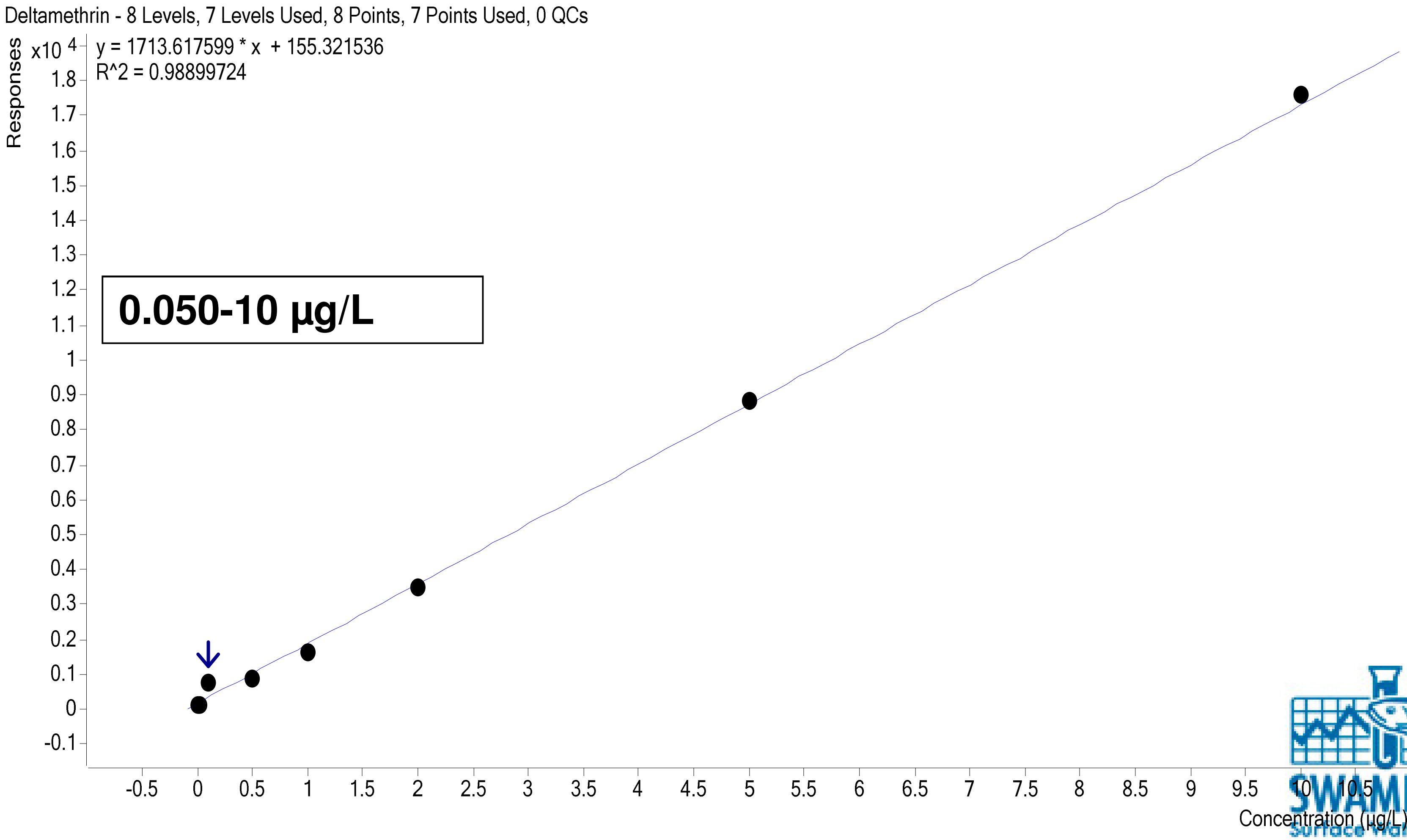
Cypermethrin MRM by NCI Ammonia



Deltamethrin MRM by NCI Methane



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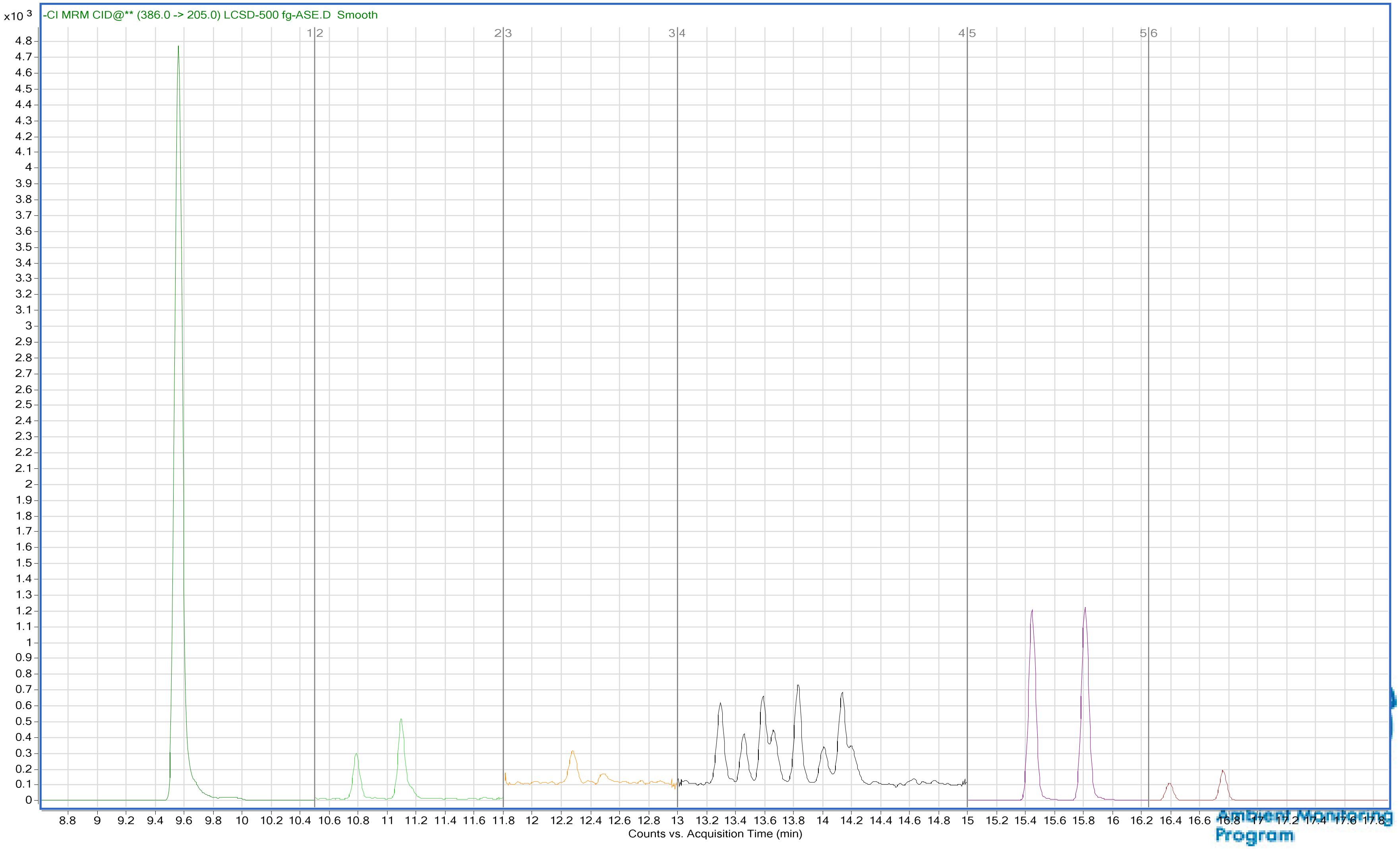
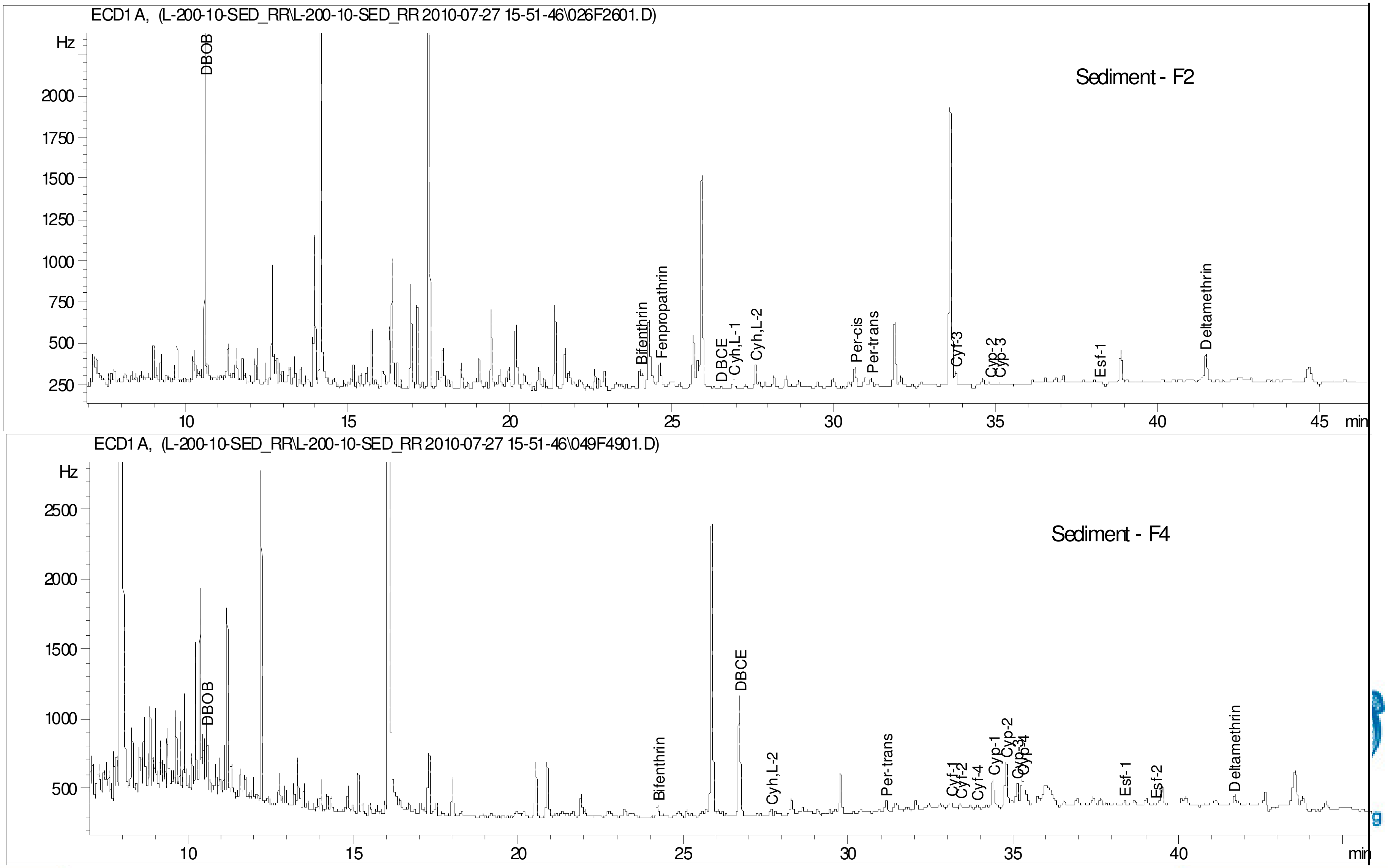
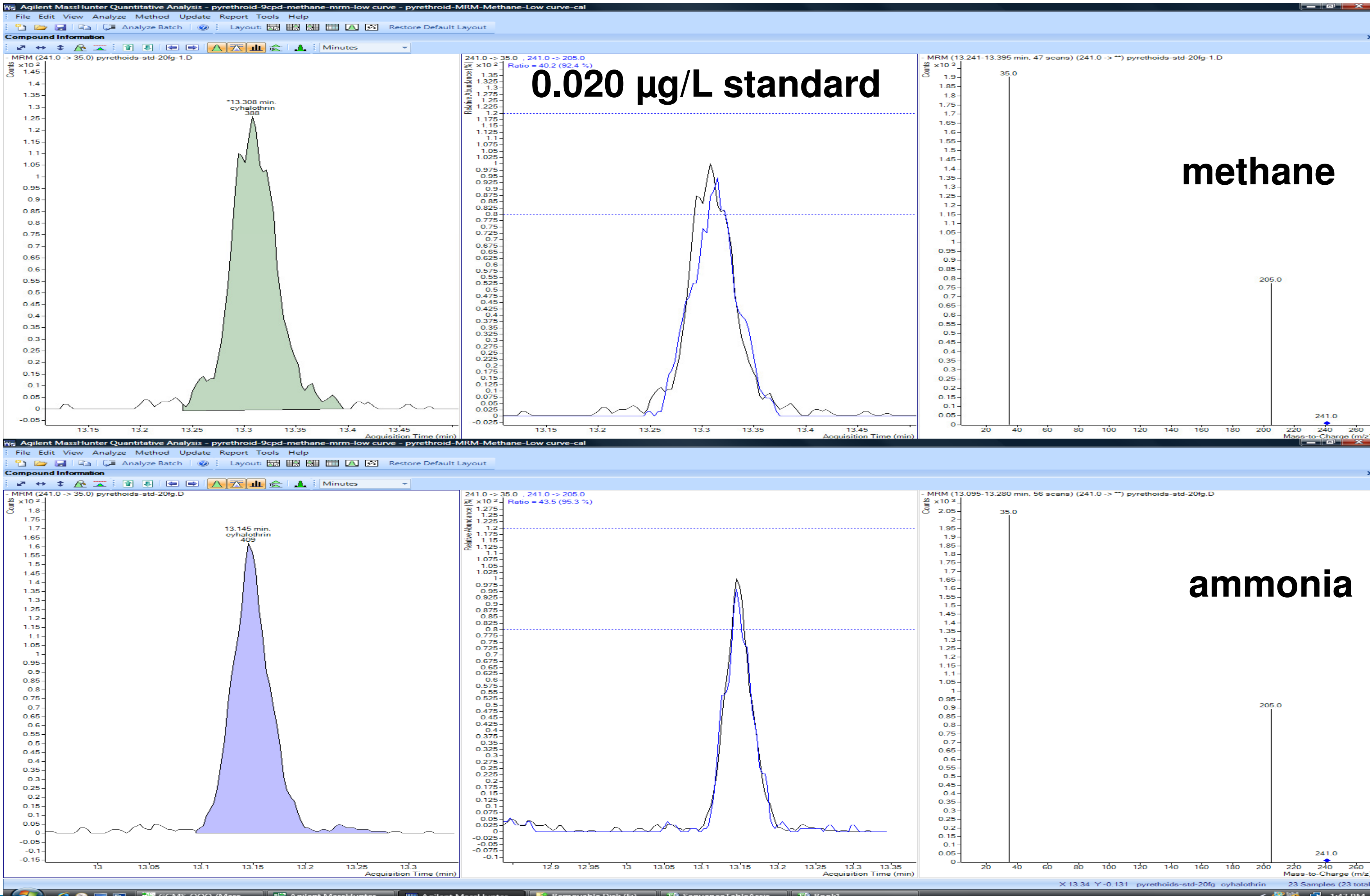
Sediment-100fg spike



GC/ECD DB5 - Sediment Extracts

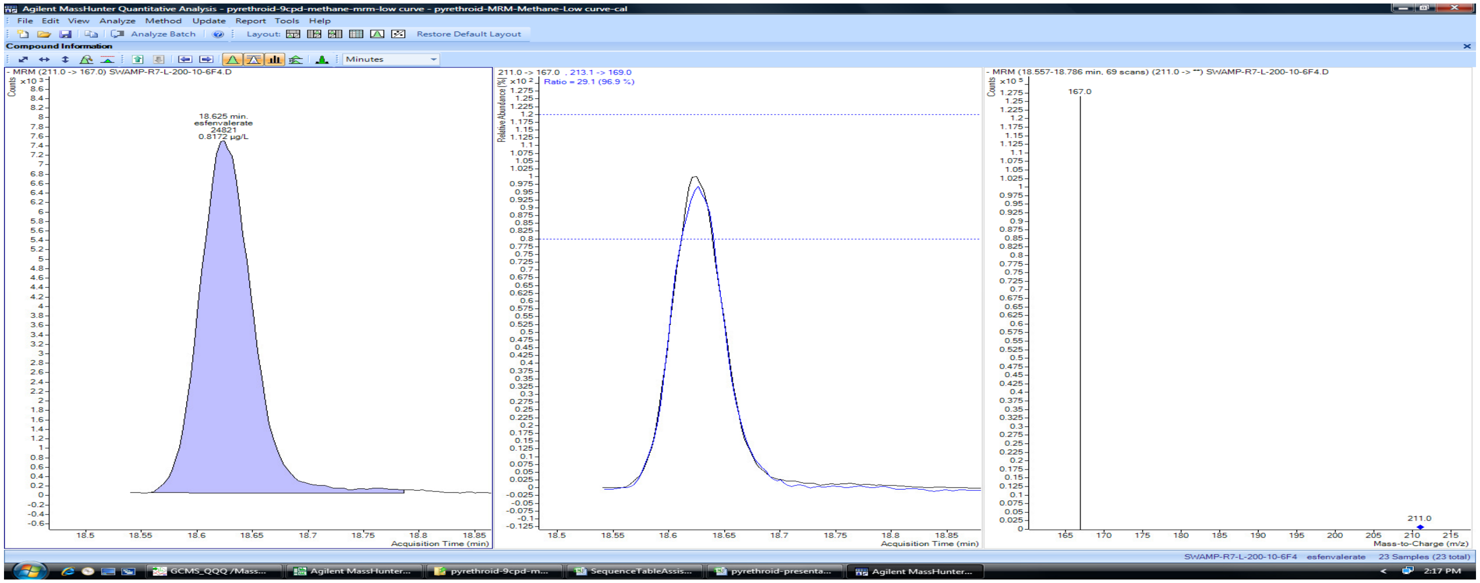


Lambda-cyhalothrin MRM-NCI-MSMS

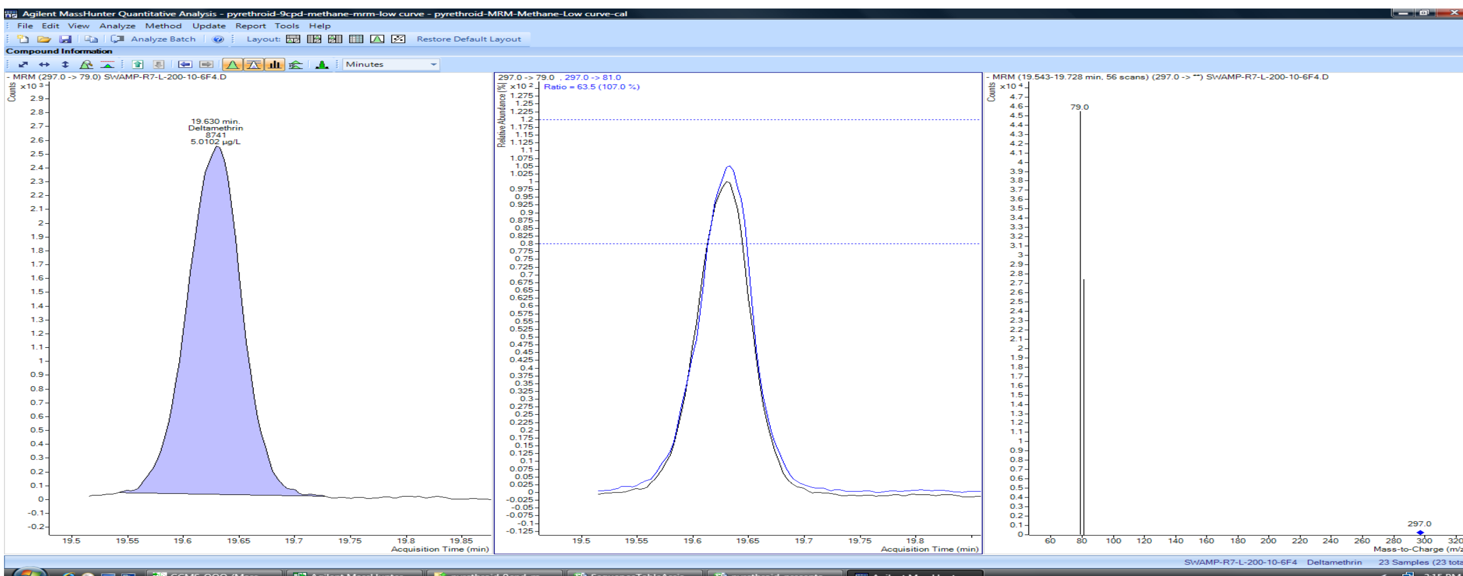


Sediment Sample Extract by NCI - methane

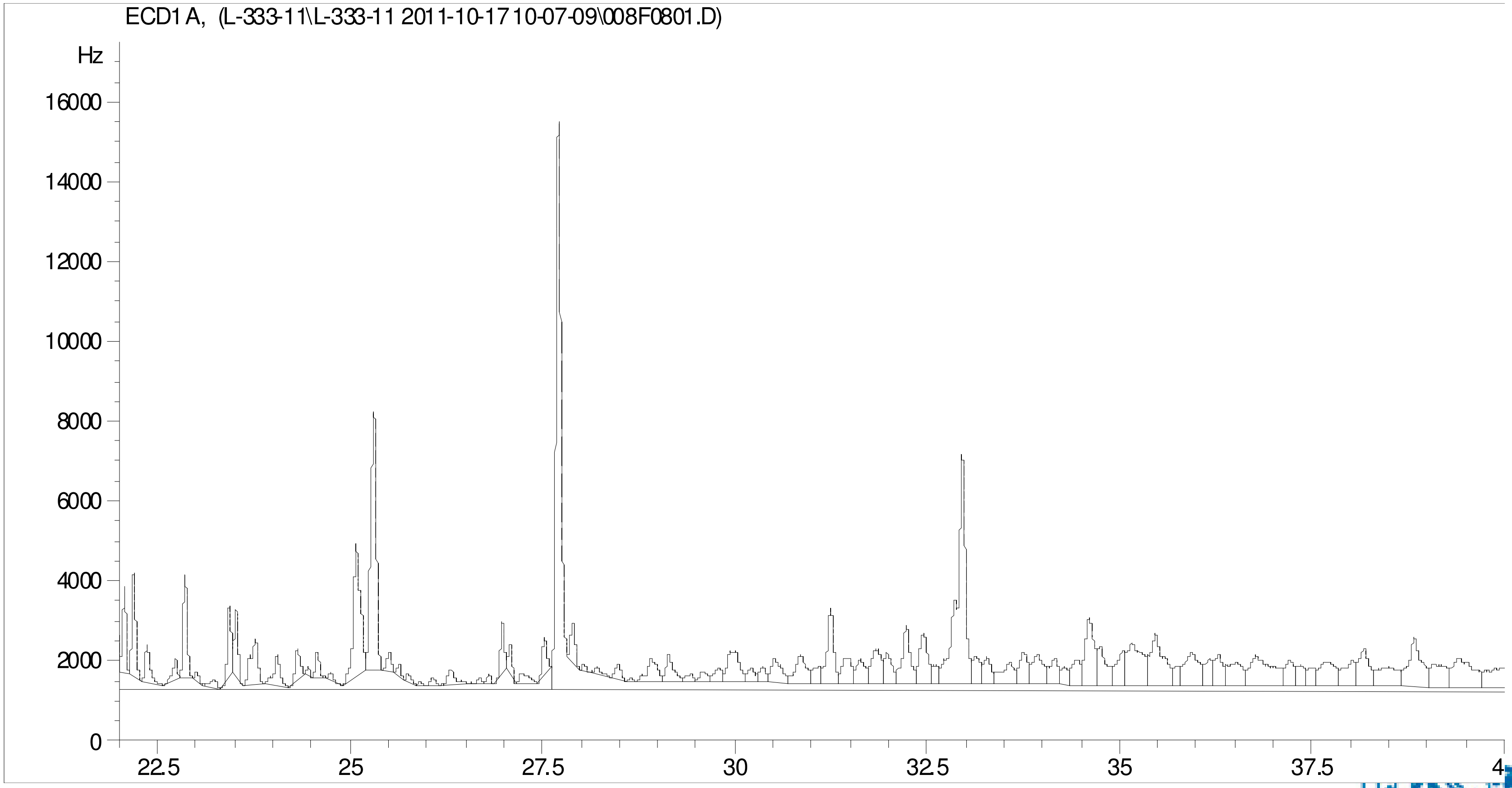
es-fenvalerate
0.81 ng/g



deltamethrin
5.01 ng/g



ECD - Round Robin Sediment Extract – 2011



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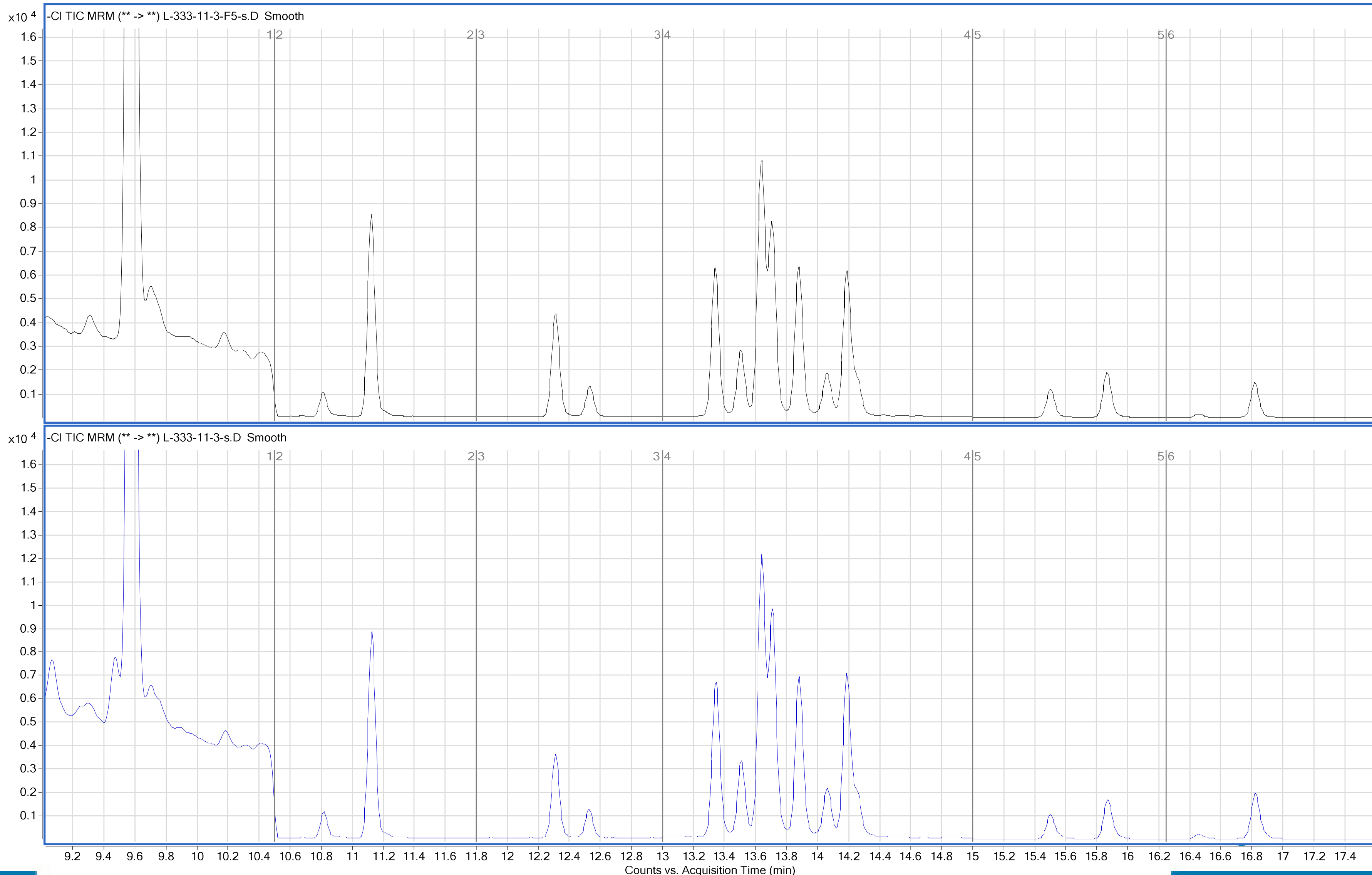
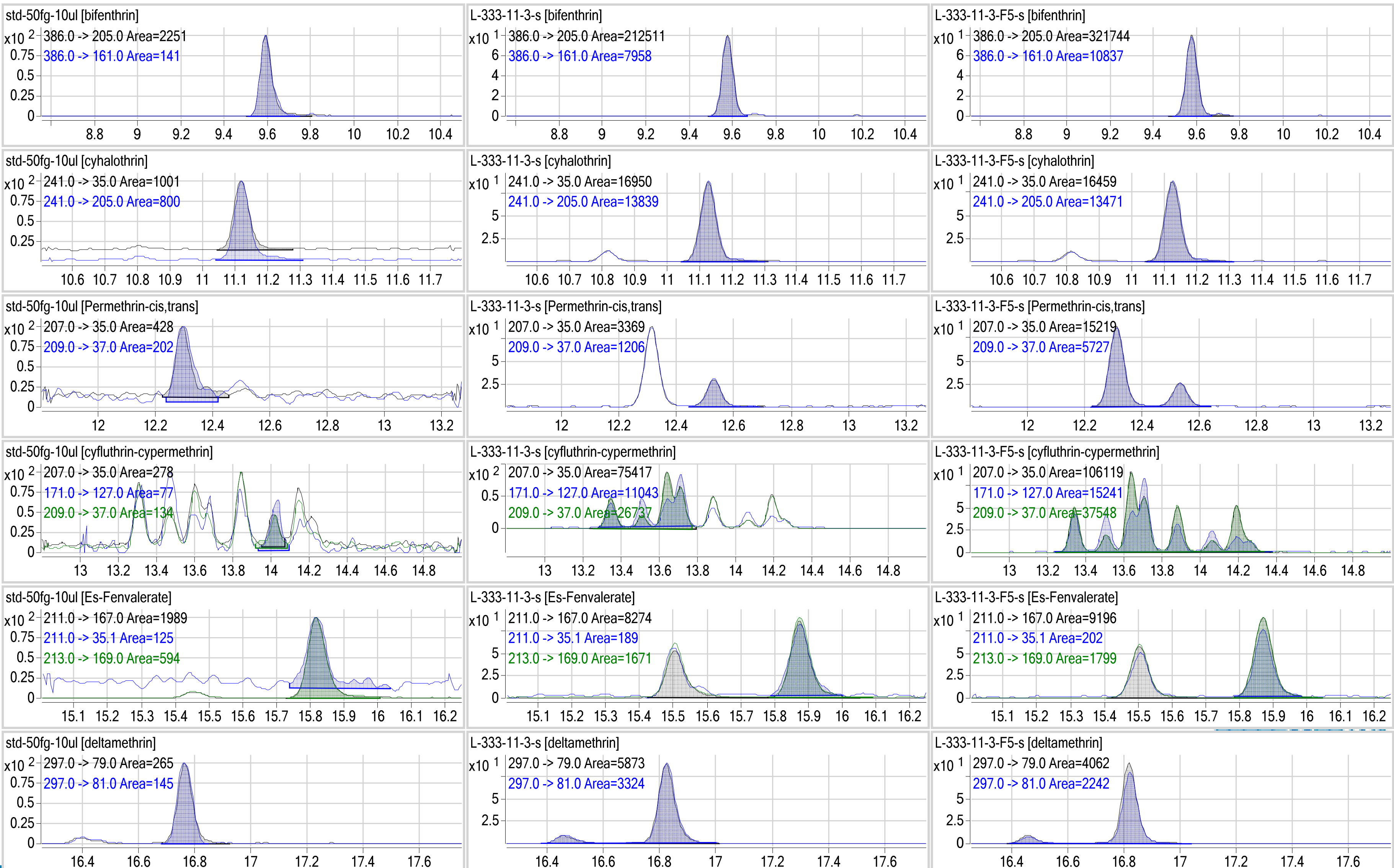
NCI - Round Robin Sediment Extract – 2011



NCI - Round Robin Sediment Extract – 2011



MS/MS-EI-Signal to Noise and ELOD

Synthetic pyrethroid	std conc µg/L	MS/MS-EI-S/N	Estimated Limit of Detection (ELOD) Sediment ng/g
Allethrin	0.500	629	1.50
Parallethrin	0.500	325	0.80
Resmethrin	0.500	501	0.80
Bifenthrin	0.500	1408	0.30
Fenpropathrin	0.500	165	1.20
Tetramethrin	0.500	262	0.50
Phenothrin	0.500	686	0.50
Cyhalothrin	0.500	197	0.35
Permethrin cis	0.500	423	0.75
Permethrin trans	0.500	362	0.95
Cyfluthrin	0.500	24.5	0.35
Cypermethrin	0.500	40.0	0.45
Es-fenvalerate	0.500	57.4	0.25
Deltamethrin	0.500	30.9	0.50

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MS/MS-NCI-Signal to Noise and ELOD

Synthetic pyrethroid	std conc µg/L	MS/MS-NCI-Signal to Noise S/N		Estimated Limit of Detection (ELOD)	
		Methane	Ammonia	Water ng/L	Sediment ng/g
Bifenthrin	0.050	973	2345	0.10	0.08
Cyhalothrin	0.050	683	1890	0.20	0.1
Permethrin	0.050	25	150	1.00	1.5
Cyfluthrin	0.050	277	1217	0.20	0.2
Cypermethrin	0.050	336	1410	0.20	0.18
Es-fenvalerate	0.050	2757	6450	0.05	0.05
Deltamethrin	0.050	190	463	0.15	0.3

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Pyrethroid Method Detection and Reporting Limits for Water, Sediment and Tissue - ECD

Sample Matrix	Water		Sediment		Tissue	
Pyrethroid Pesticides	MDL ppb (ug/L)	RL ppb (ug/L)	MDL Dry wt ppb (ng/g)	RL Dry wt ppb (ng/g)	MDL Fresh wt ppb (ng/g)	RL Fresh wt ppb (ng/g)
Bifenthrin	0.001	0.002	0.50	1.00	0.65	2.00
Cyfluthrin	0.002	0.004	2.00	4.00	2.70	6.00
Cypermethrin	0.004	0.004	2.00	4.00	1.70	4.00
Deltamethrin	0.002	0.004	2.00	4.00	0.60	2.00
Es/Fenvalerate	0.001	0.002	1.00	2.00	1.70	4.00
Fenpropathrin	0.002	0.004	2.00	4.00	1.35	4.00
Lambda-cyhalothrin	0.001	0.002	1.00	2.00	1.50	4.00
Permethrin	0.003	0.005	4.00	8.00	2.20	6.00

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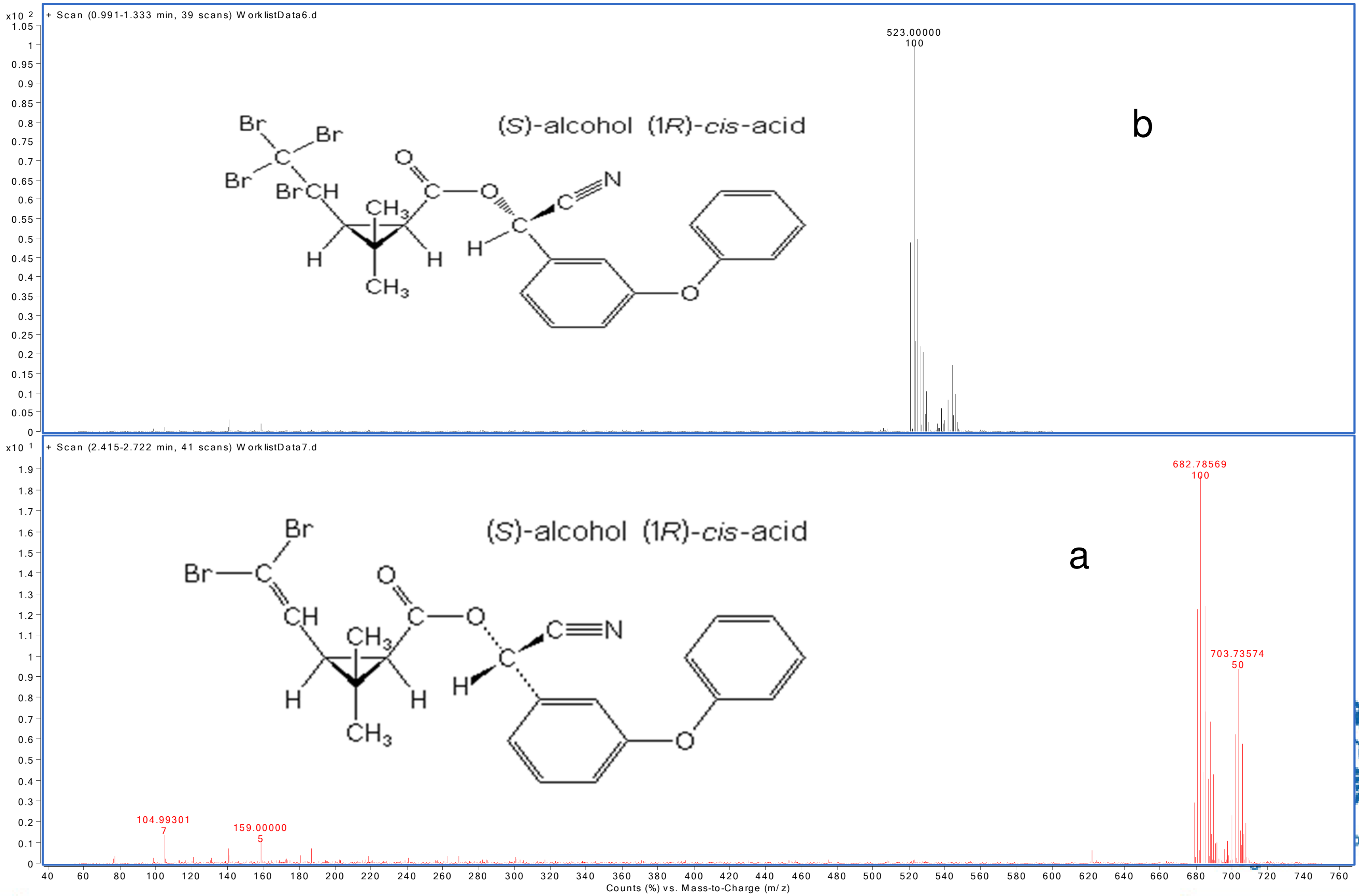
Analysis of Deltamethrin(a) and Tralomethrin(b) using LC/MS



Conclusions

- Analysis of pyrethroids by GC-MSMS-NCI yields low detection limits that are necessary for toxicity of these analytes
- GC-NCI-MSMS is at least 5 times more sensitive than GC-EI-MSMS but is not suitable for all pyrethroid pesticides
- Ammonia NCI is 5-10 times more sensitive than methane
- LC-MS is necessary to distinguish between deltamethrin and tralomethrin

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Thank You

Any questions?

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