


Screening of Emerging Contaminants in Water by HRAM MS

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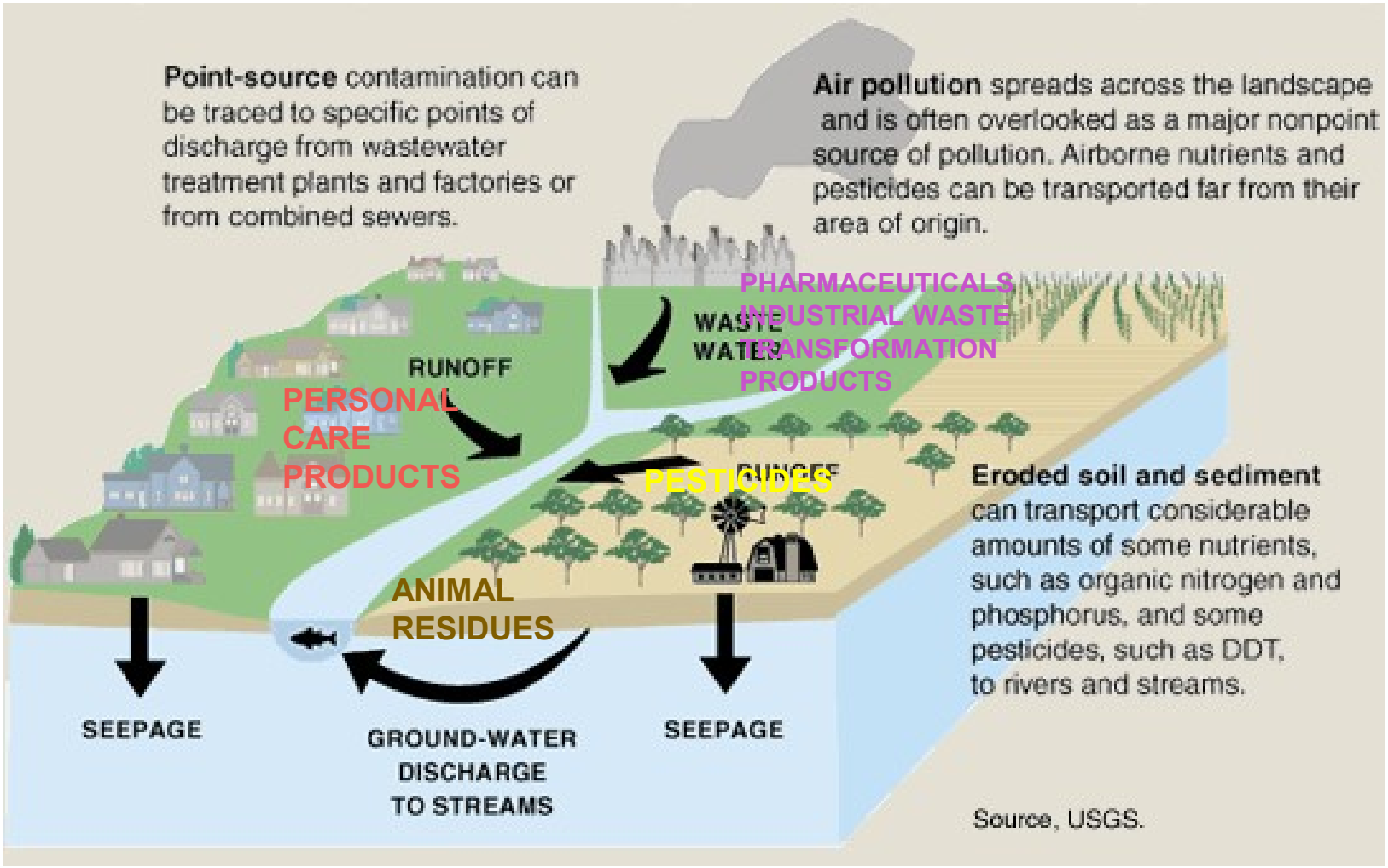
WATER CONTAMINATION



Water Contamination
Media and Public Awareness


More health news on NBCNEWS.com

Pharmaceuticals lurking in U.S. drinking water

AP probe found traces of meds in water supplies of 41 million Americans

The Washington Post

Energy and Environment

Pesticides are polluting our waters — and we often don't know it

Fracking Chemicals Detected in Pennsylvania Drinking Water

By NICHOLAS ST. FLEUR MAY 4, 2015

The New York Times

Fears About Water Supply Grip Village That Made Teflon Products

Water Contaminants

Pain Points for Analysis

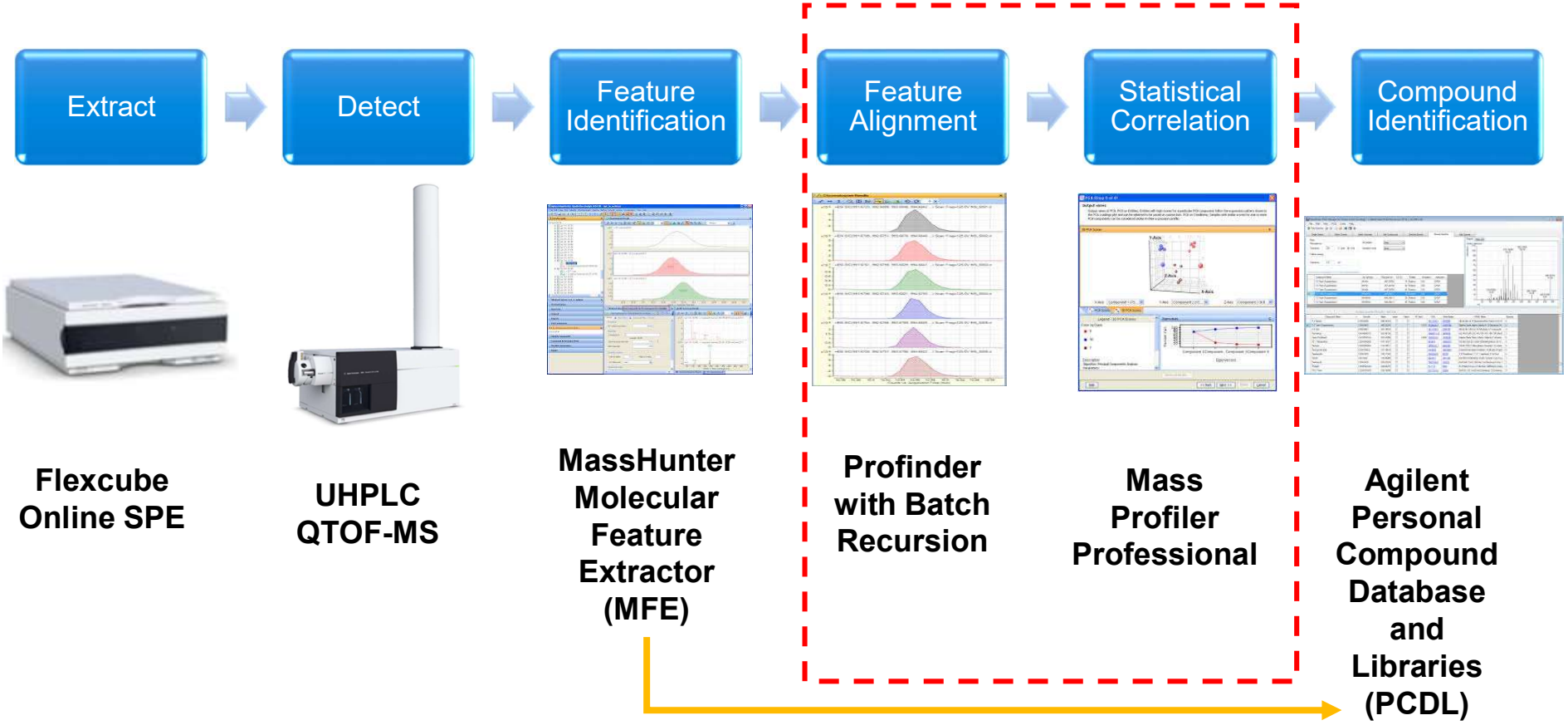
Compounds to monitor

Sample Preparation

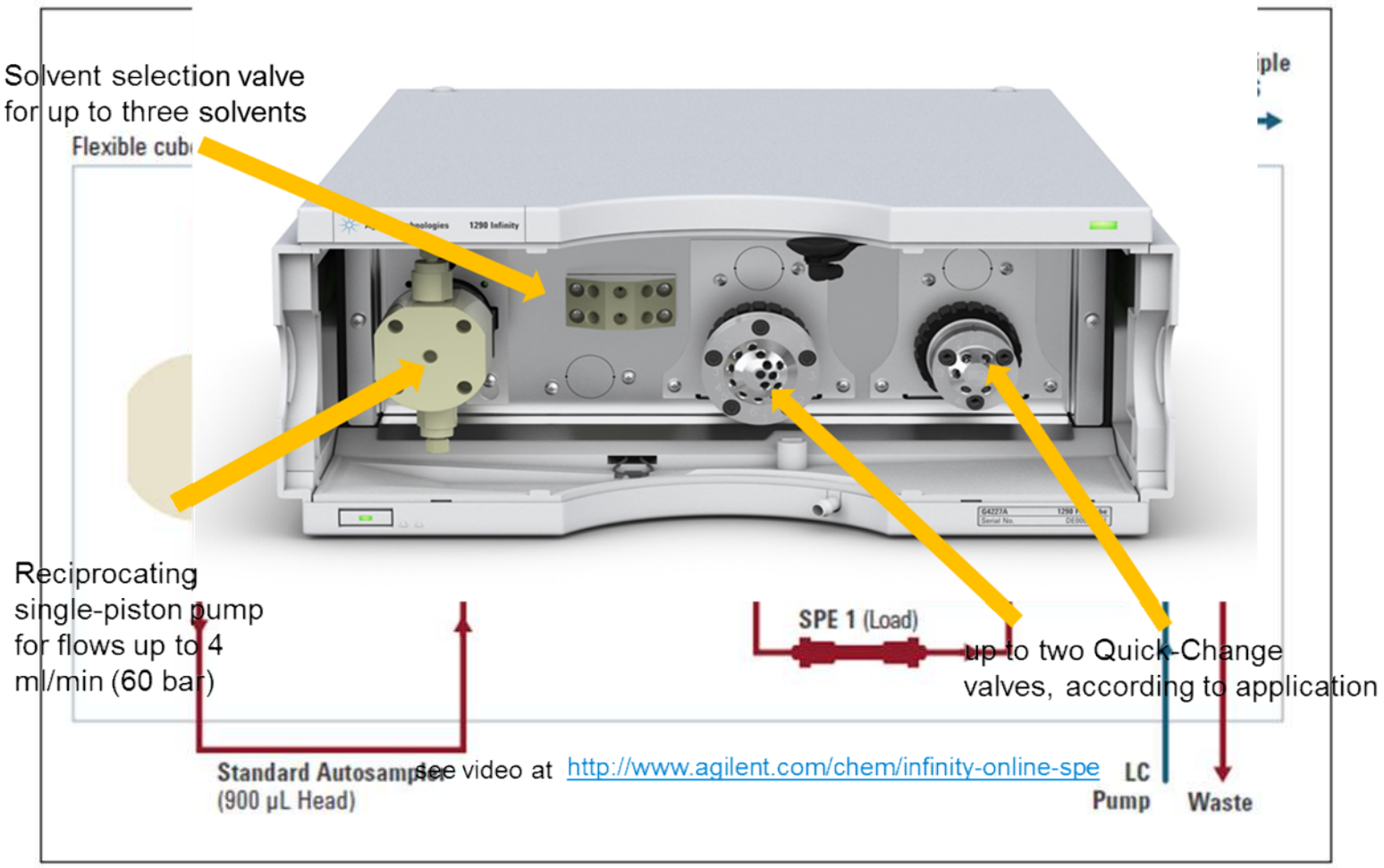
Standard Preparation

Data Analysis and Interpretation

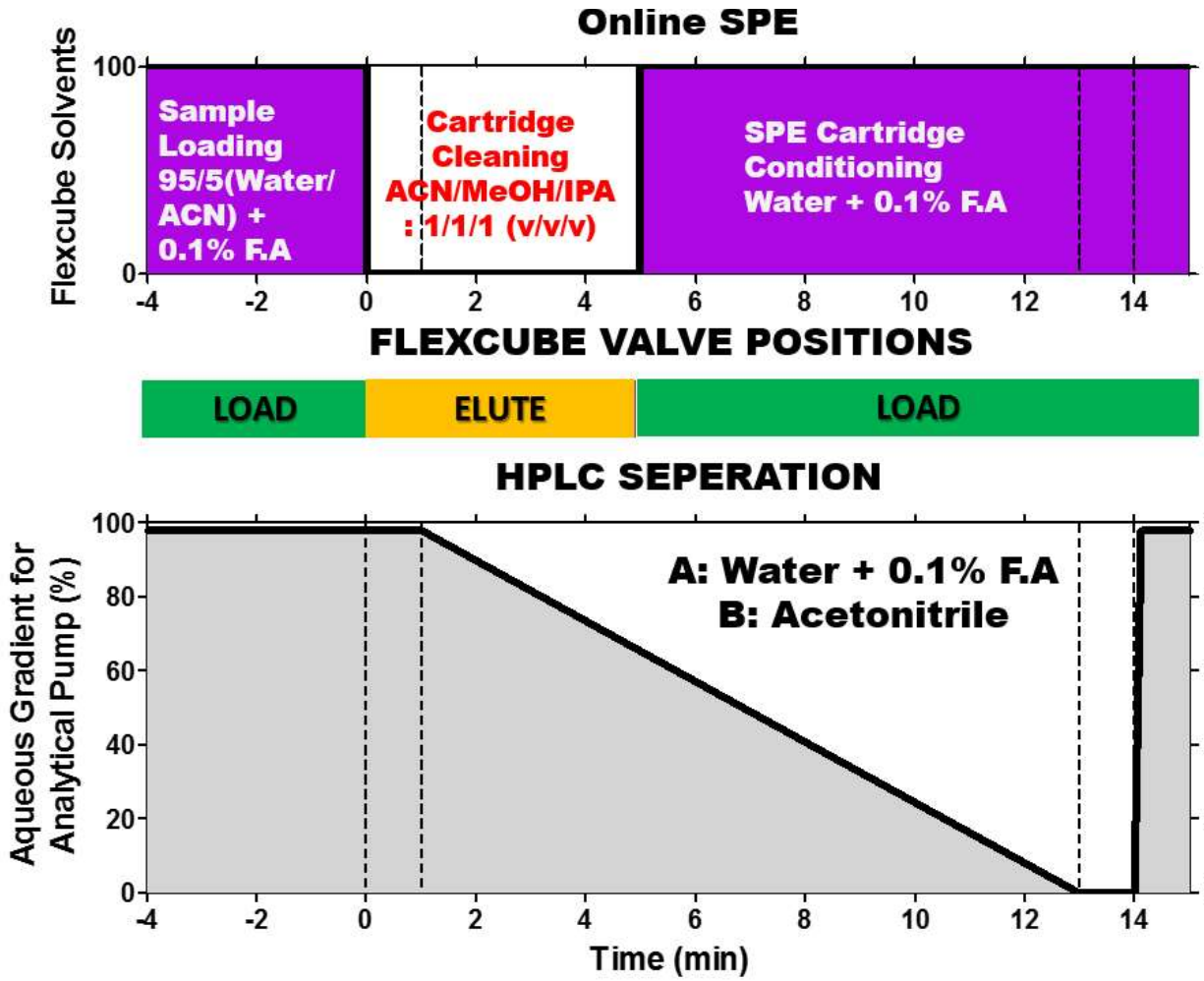
Sample Analysis - Workflow



Automated Solid Phase Extraction Flexcube



Method Parameters
Flexcube + LC



SPE Cartridge: PLRP-s, 2.1x12.5 mm
Flowrate: 1 mL/min

Column: Poroshell EC 120 C-18, 2.1x100 mm (2.7 µm)
Flowrate: 0.35 mL/min
Injection Volume: 900 µL

Method Parameters
6550 QTOF-MS

Parameter	Condition
Instrument	Agilent 6550 Accurate-Mass QToF-MS with iFunnel technology
Ionization Mode	Positive electrospray ionization with dual jet stream
Instrument Mode	2 GHz extended dynamic range
Instrument Tune Range	Classic tune (m/z: 50-1700)
Mass Range	m/z: 50-1000
Drying Gas Temperature	130 ºC
Drying Gas Flow	16 L/min
Sheath Gas Temperature	375 ºC
Sheath Gas Flow	11 L/min
Nebulizer Gas	35 psi
Fragmentor	365 V
Capillary	3500

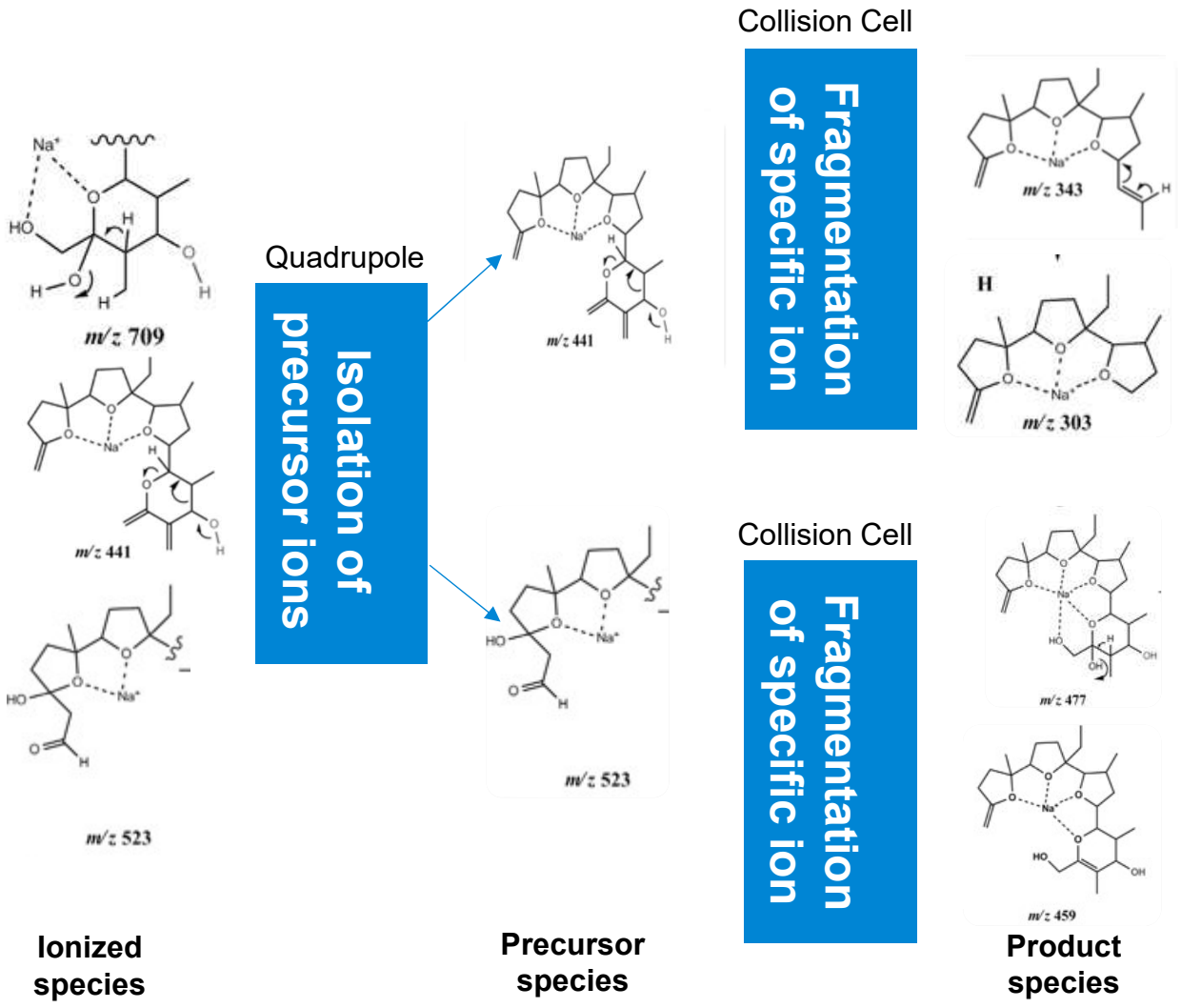
Agilent 6550 LC-QTOF MS

iFunnel Technology

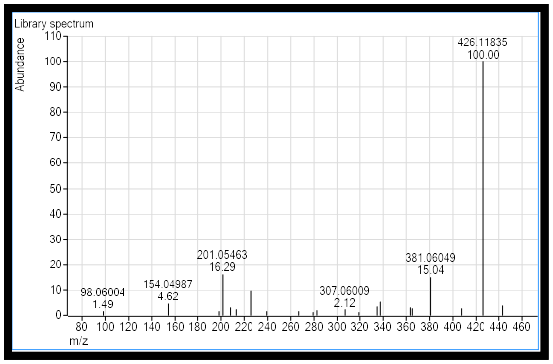
- **5-10x increase in ions sampled**
- **Enhanced sensitivity**

Analysis of Emerging Compounds

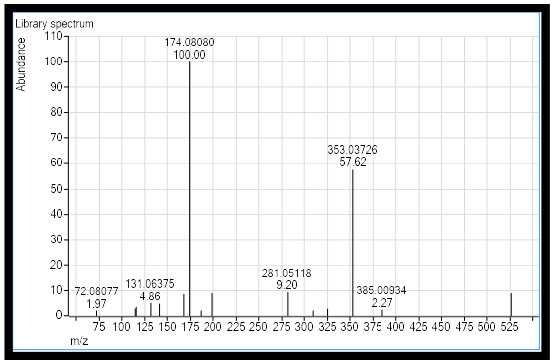
Traditional MS/MS



Individual MS/MS Spectrum

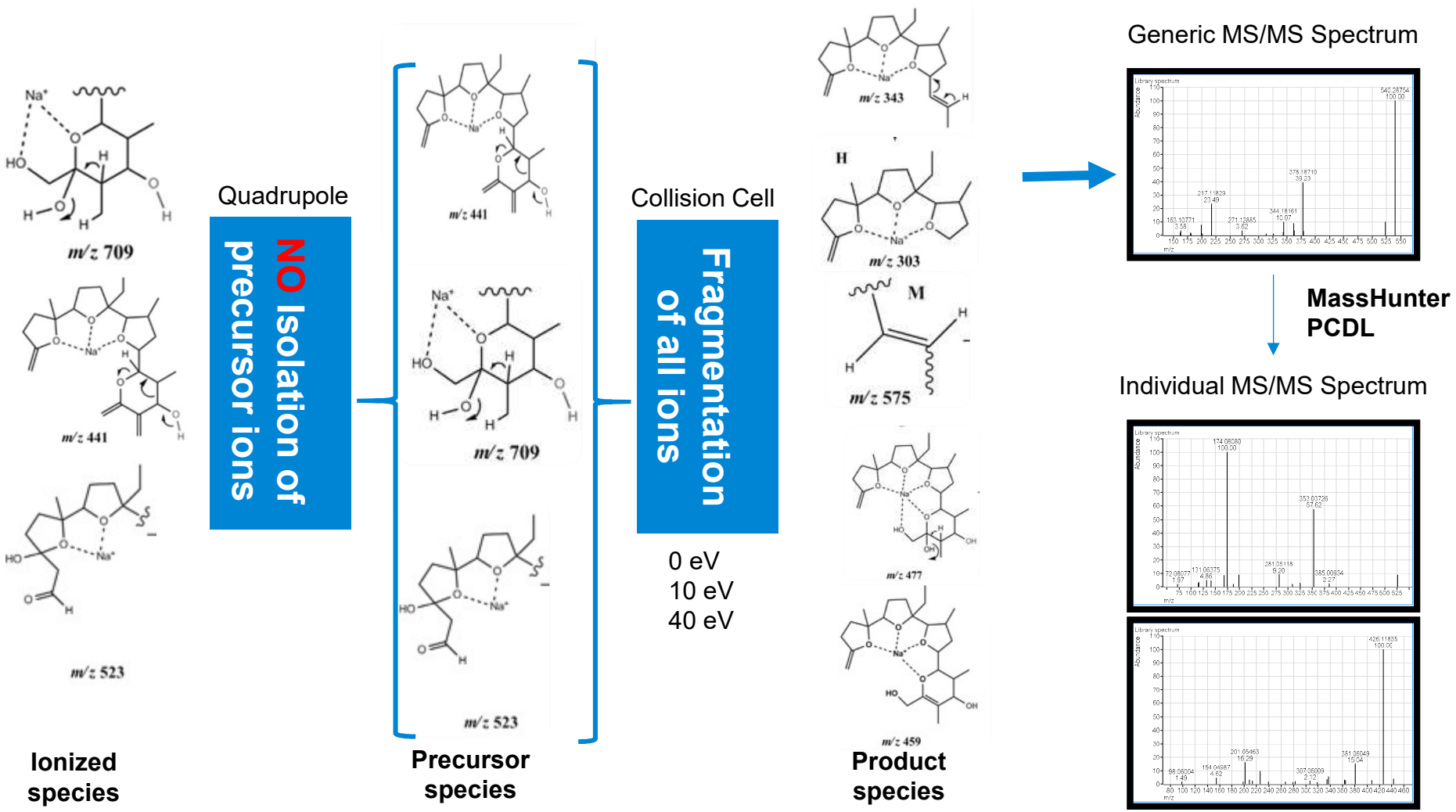


Individual MS/MS Spectrum



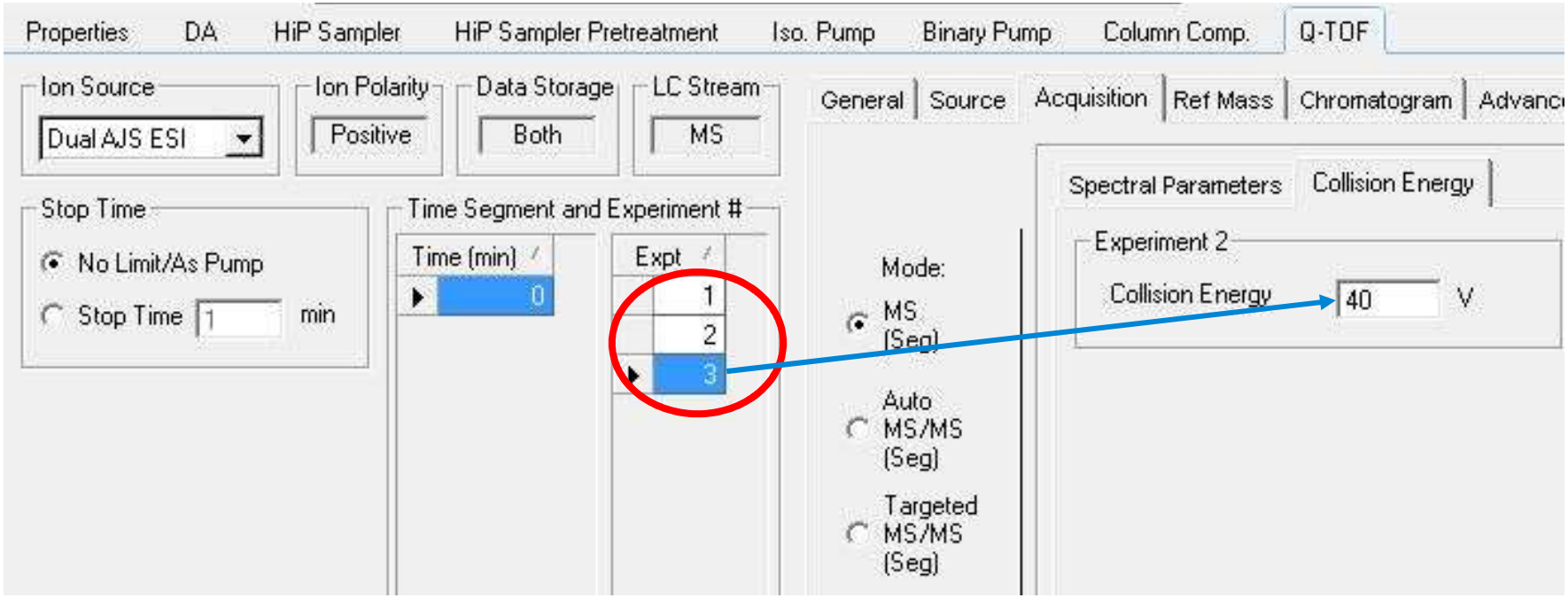
Analysis of Emerging Compounds

All Ions MS/MS



Analysis of Emerging Compounds

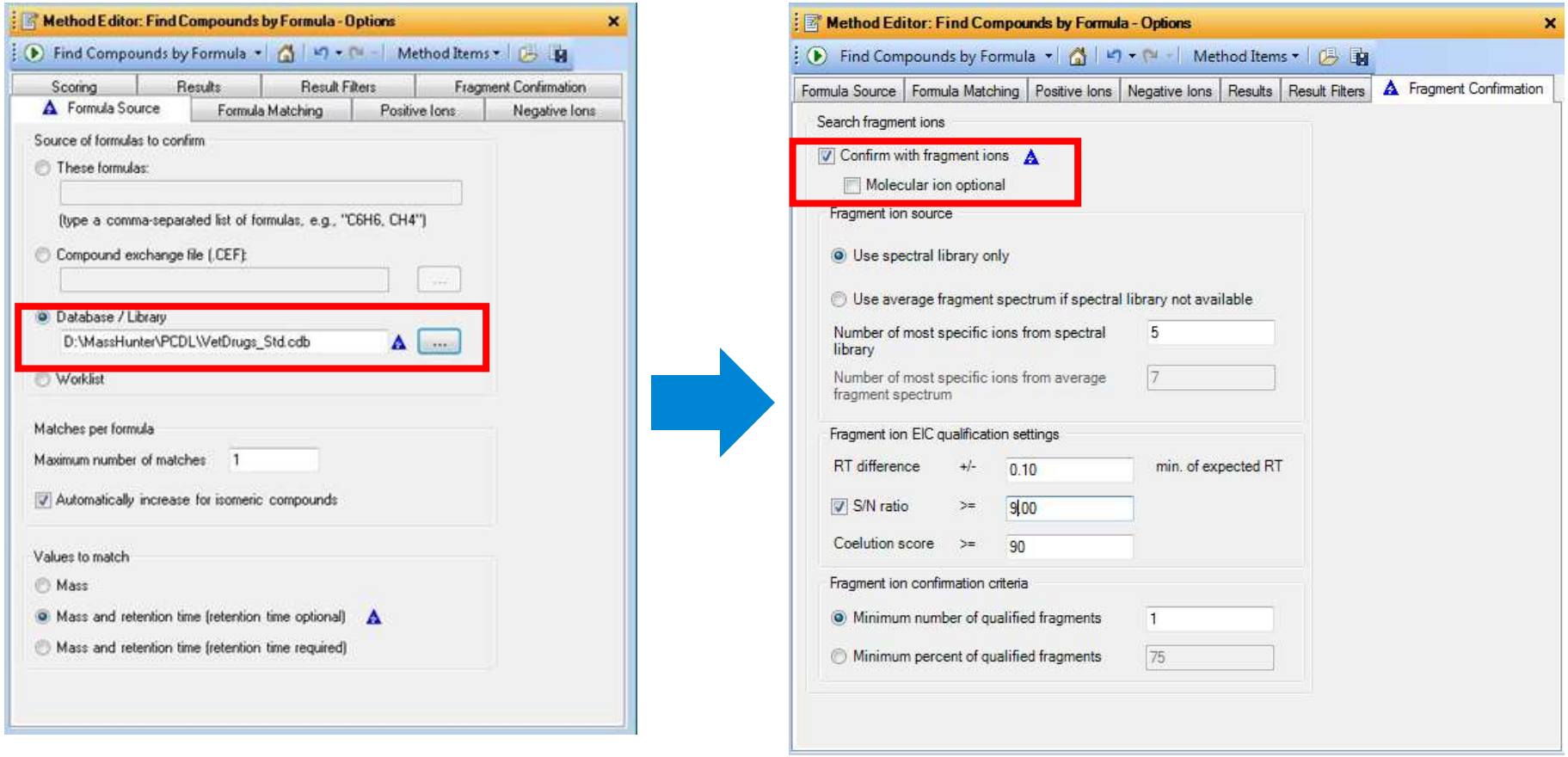
All Ions MS/MS Data Acquisition



- Three Collision energy experiments performed simultaneously at 0, 10 & 40 eV
- Spectral acquisition at 4.5 spectra/sec

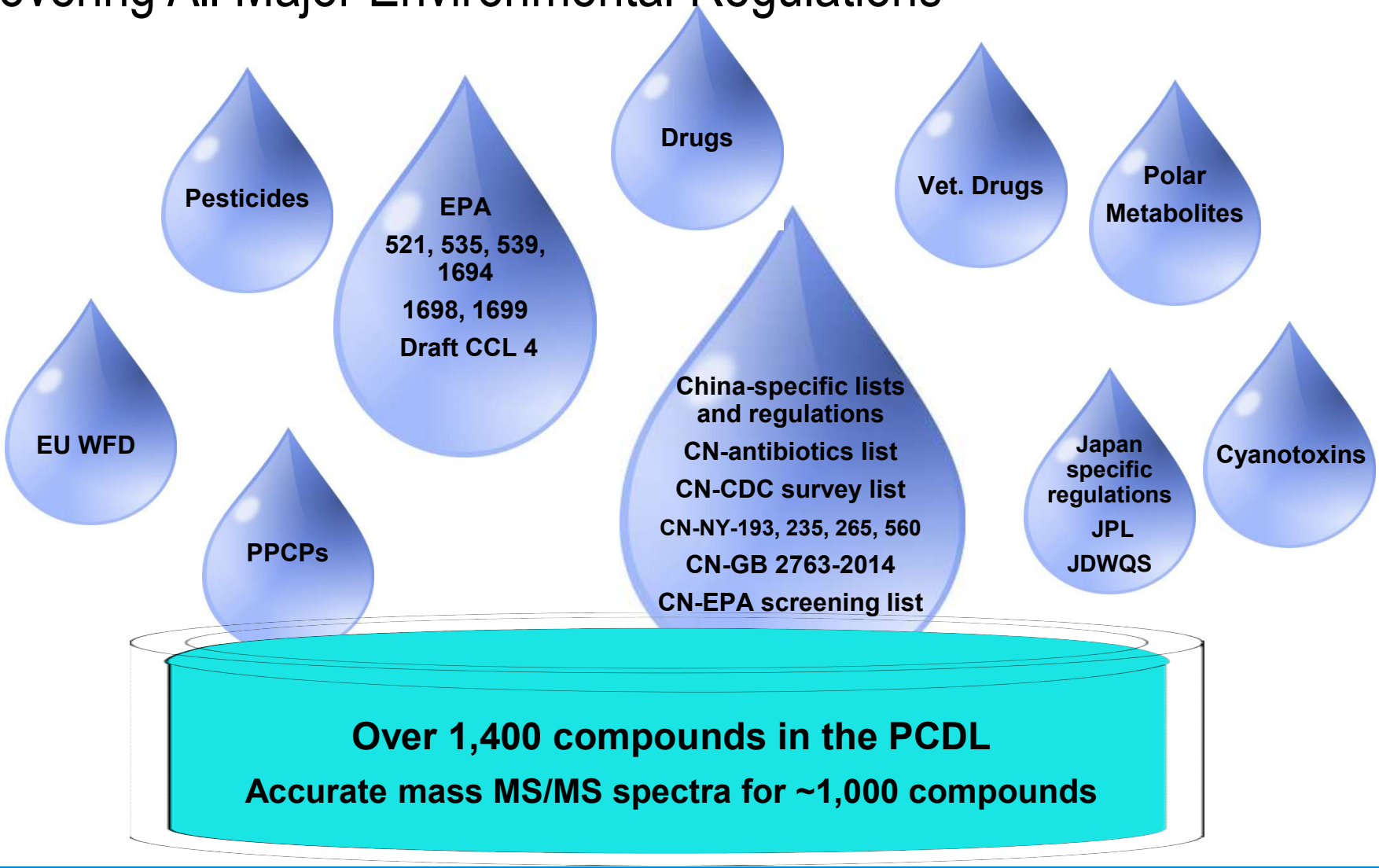
All Ions MS/MS

Workflow – Find By Formula



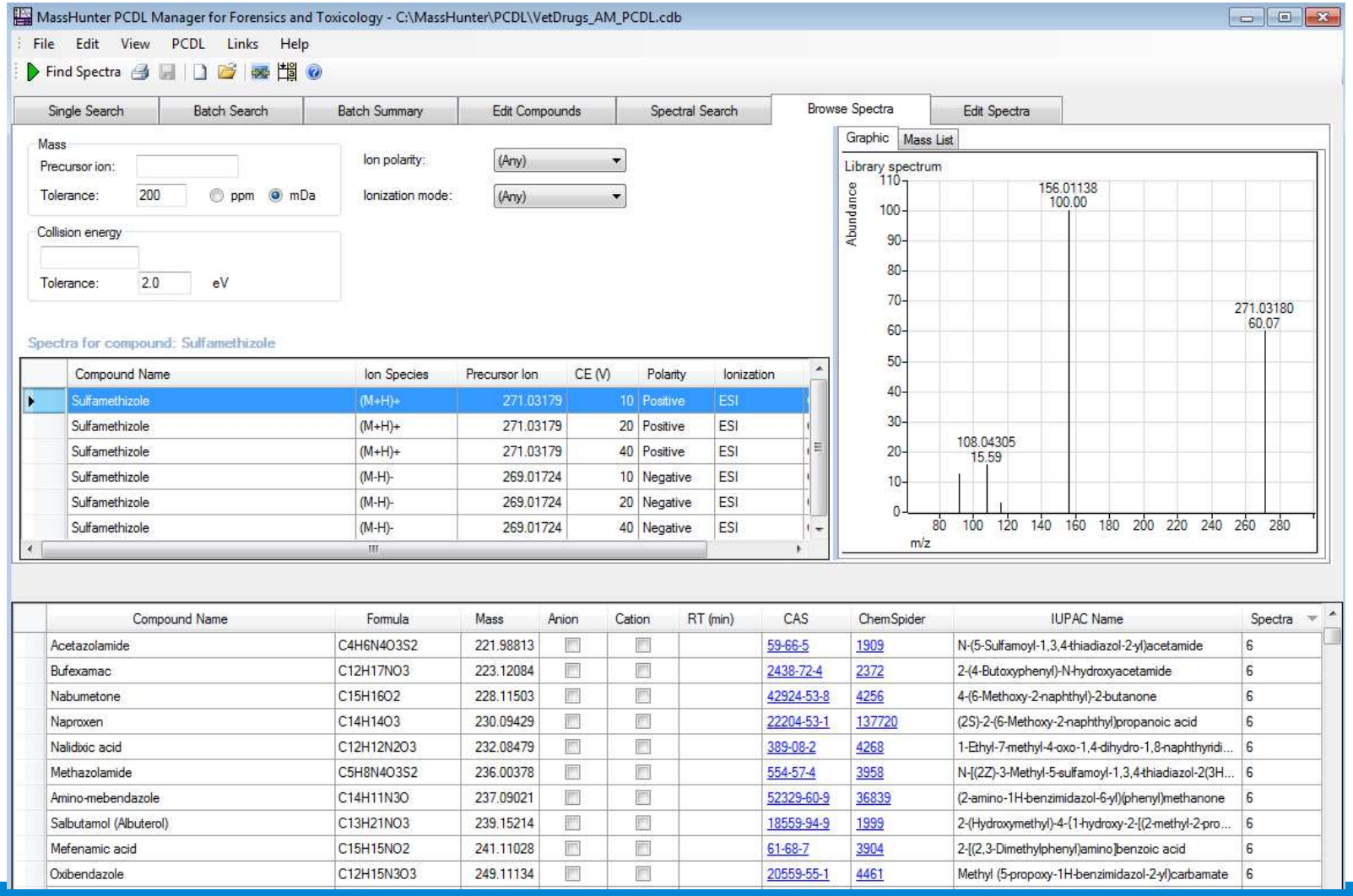
Water Screening PCDL

Covering All Major Environmental Regulations



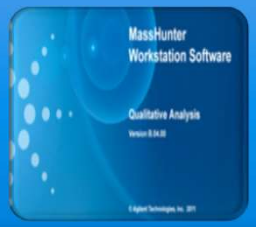
Analysis of Emerging Contaminants

Personal Compound Database and Library (PCDL)



Analysis of Veterinary Drugs in Meat

All Ions MS/MS Method Conditions

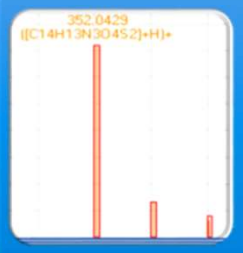


Find by Formula

- Database/Library Search
- Water Contaminant PCDL

Precursor Identification

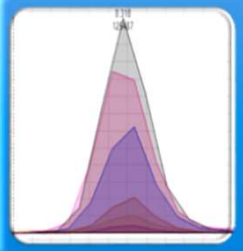
- Mass Tolerance: 10 ppm
- Retention Time Tolerance: 0.2 min
- Minimum Absolute Area Counts: 10,000



Molecular-Ion Assesment

- **Mass accuracy**
- **Isotope abundundence**
- **Isotope spacing**

- **Warn if <85.0** Reject if <50.0

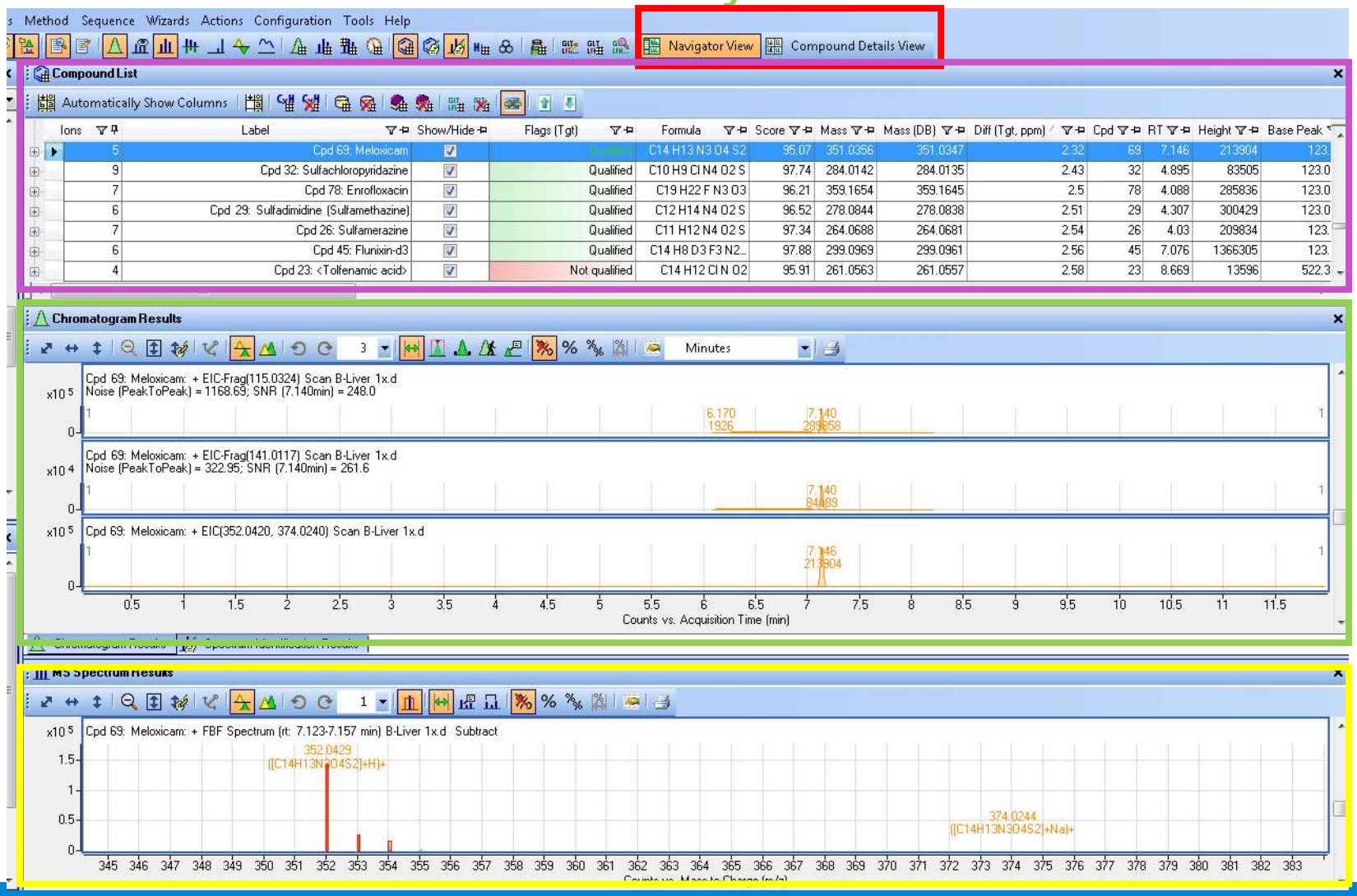


Fragment Confirmation

Min. Number of fragments req.: 1
Minimum S/N: 9.0
Coelution score: >90.0

Analysis of Water Contaminants

All Ions MS/MS Data Analysis



Analysis of Water Contaminants

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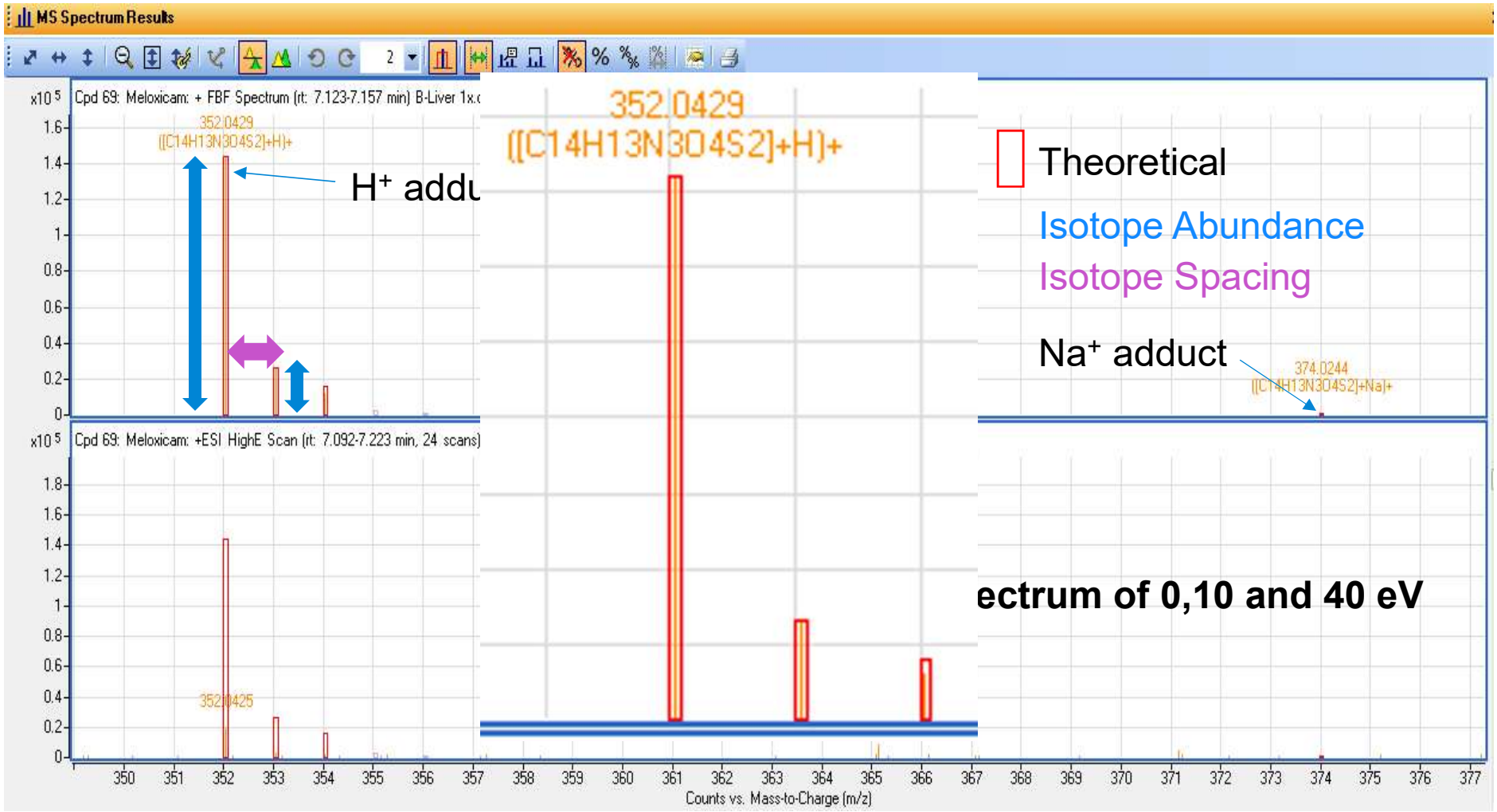
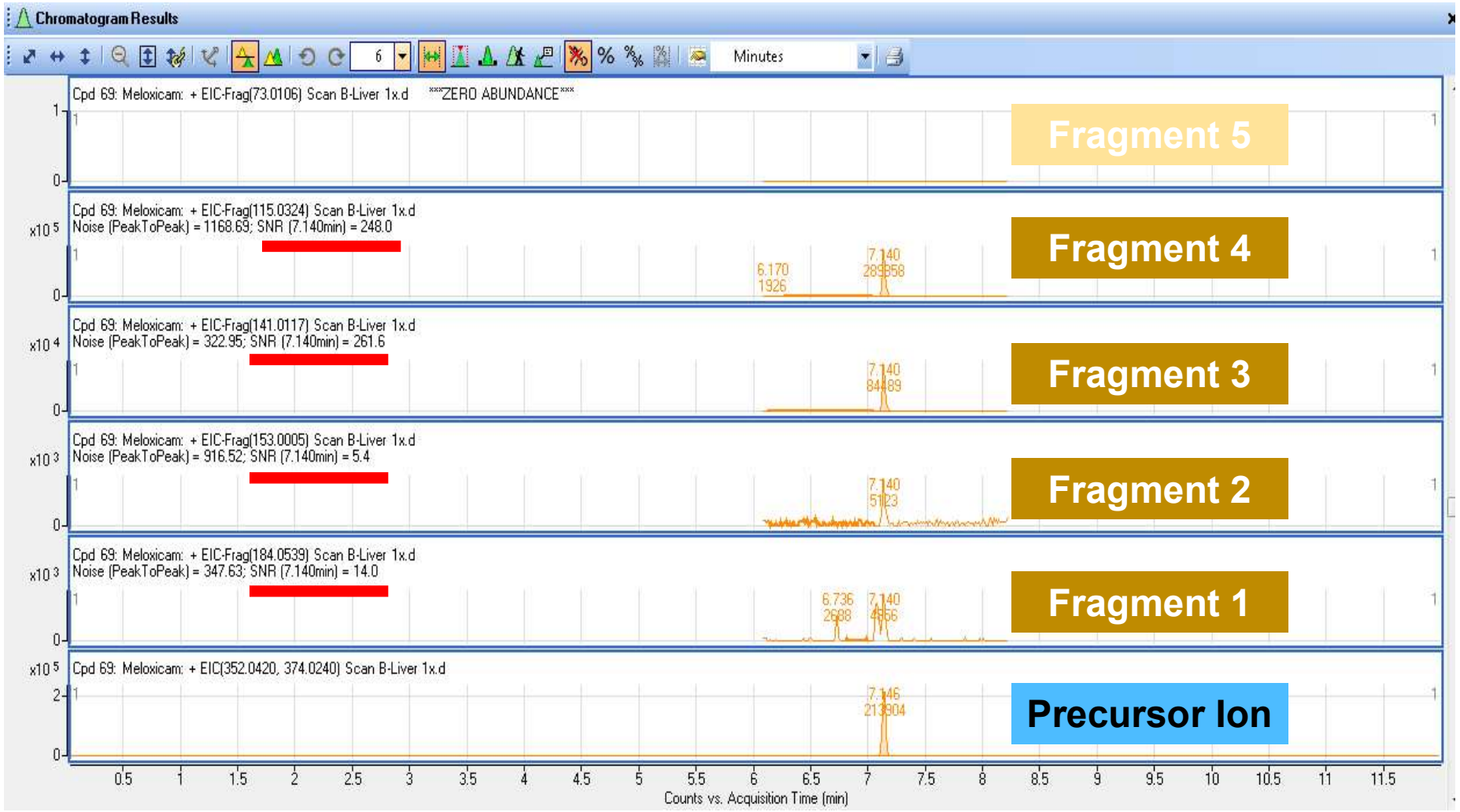


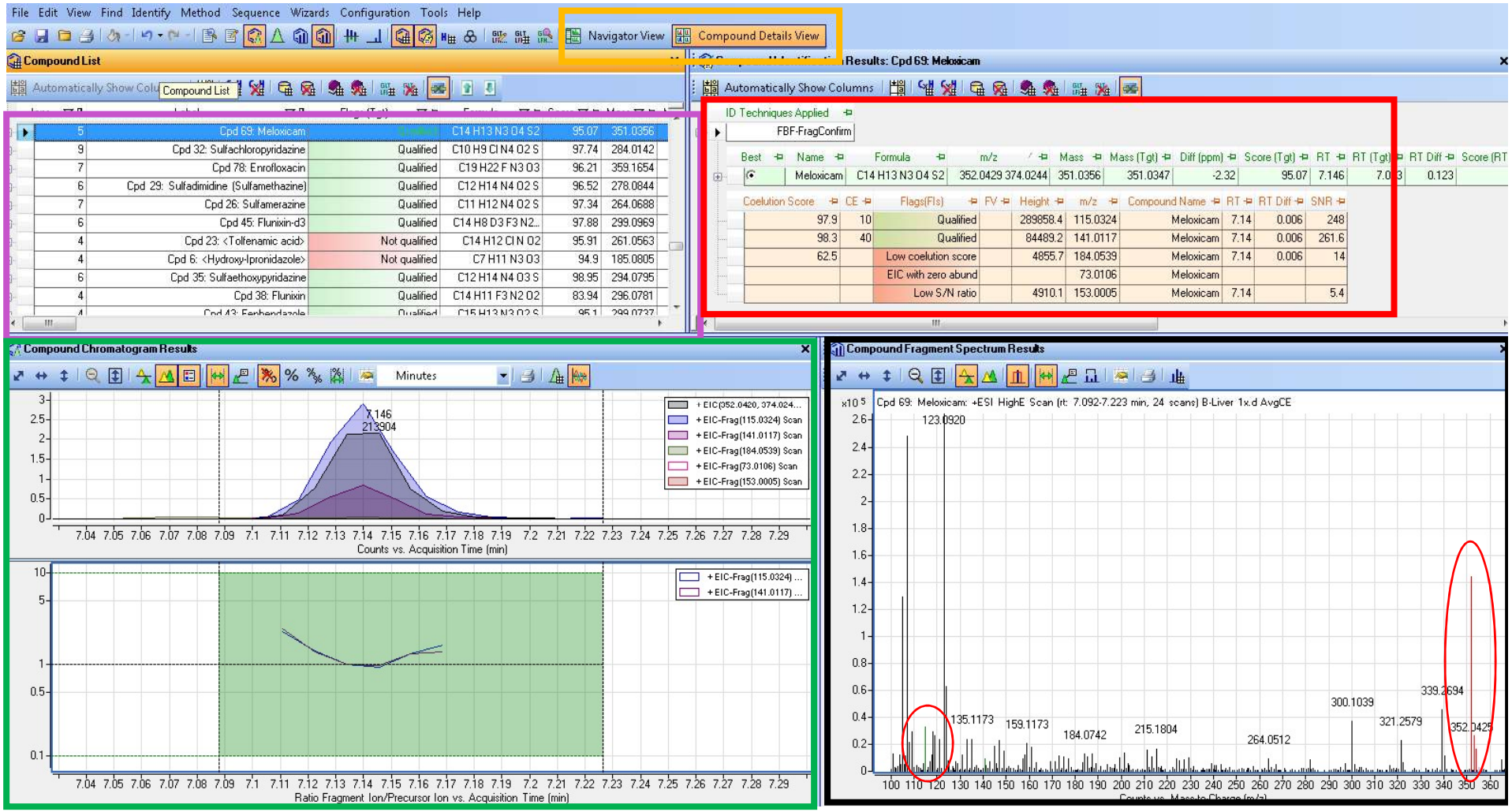
Analysis of Water Contaminants

All Ions MS/MS Data Analysis

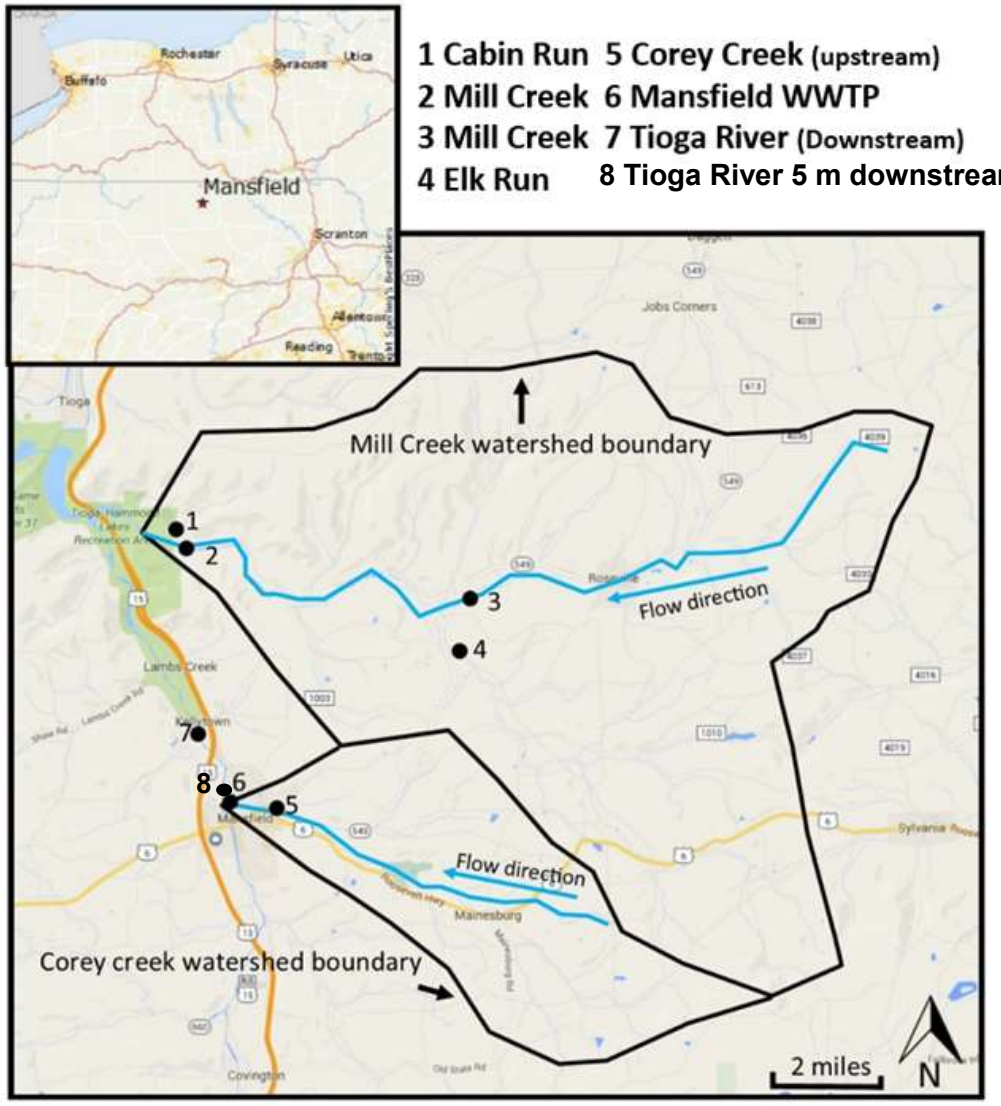


Analysis of Water Contaminants

All Ions MS/MS Data Analysis



Sampling Locations

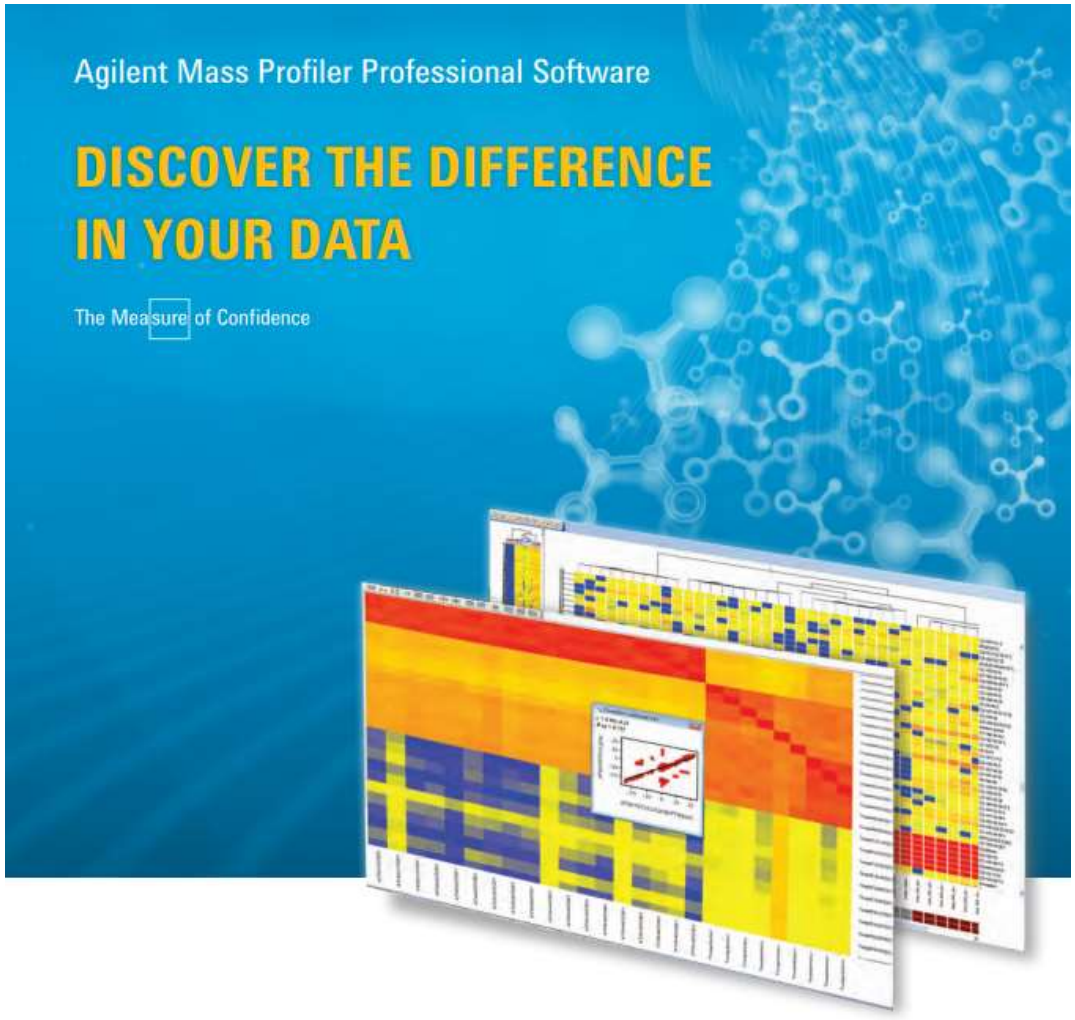


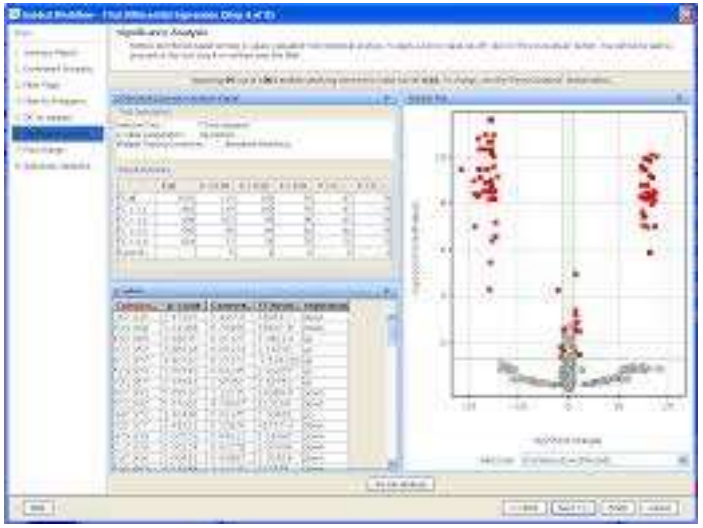
Mill Creek (1-4) and Corey Creek (5) are tributaries of the Tioga River (7) which discharges into the Susquehanna River. The River serves as a source of drinking water to 4.1 million people in NY, PA and MD.

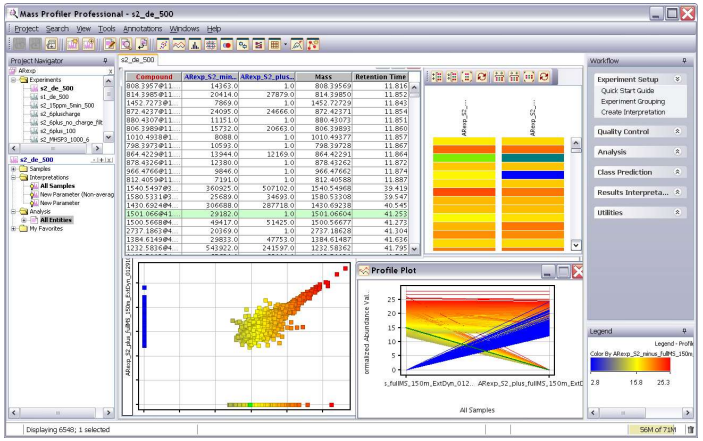
SAMPLE COLLECTION

40 mL samples collected in amber glass vials and shipped to the lab on ice within 24 hours.

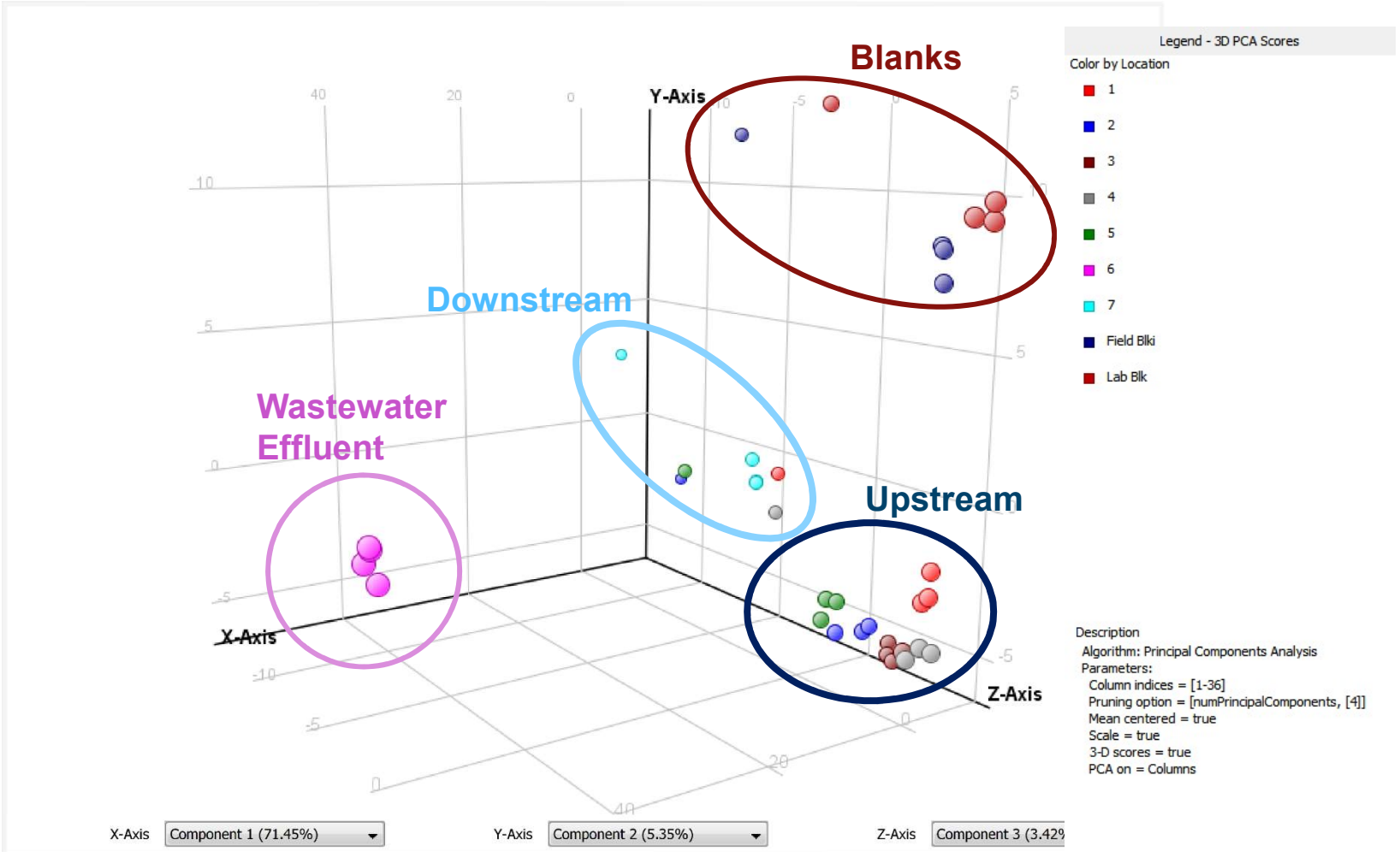
Statistical Differentiation of Samples
Mass Profiler Professional



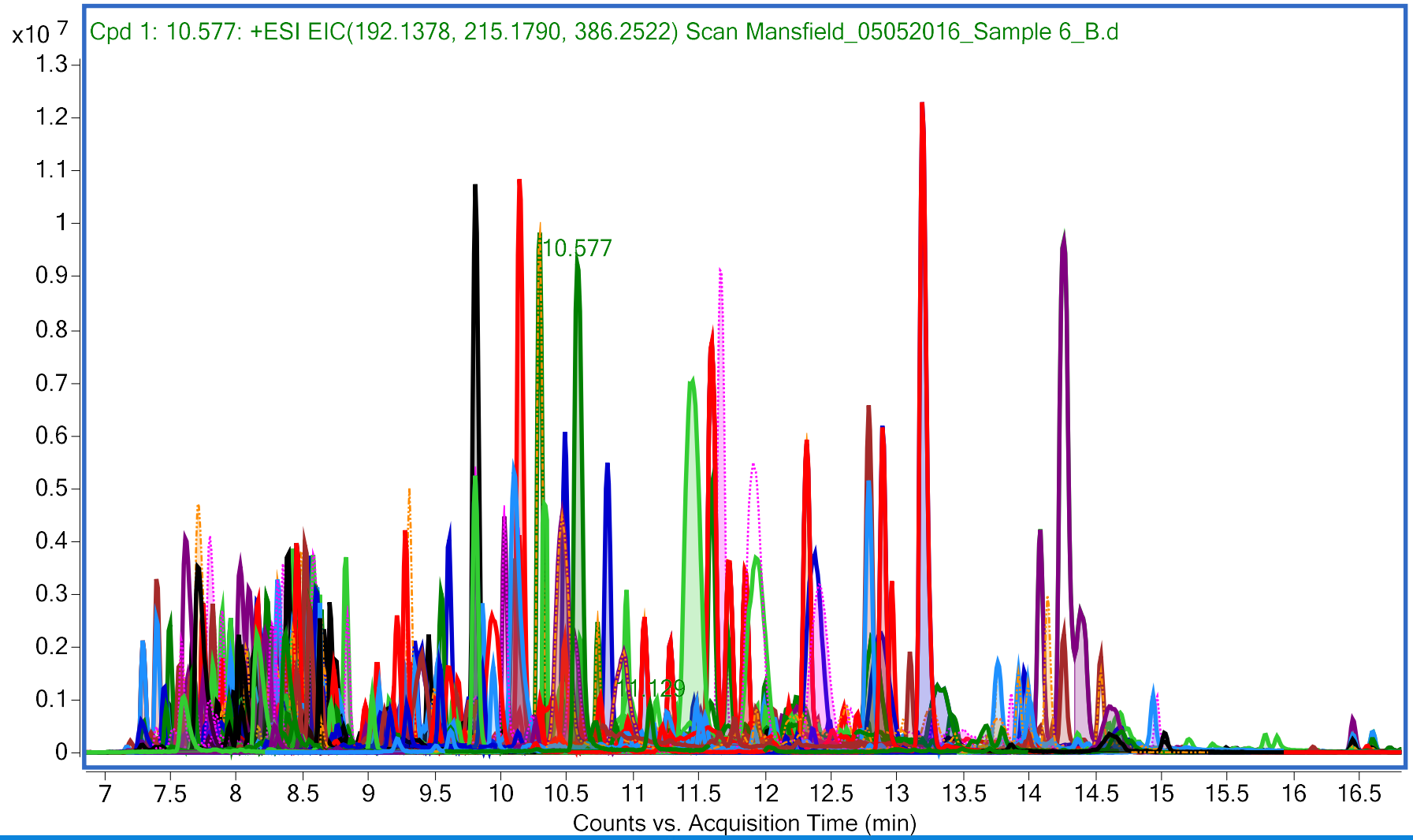




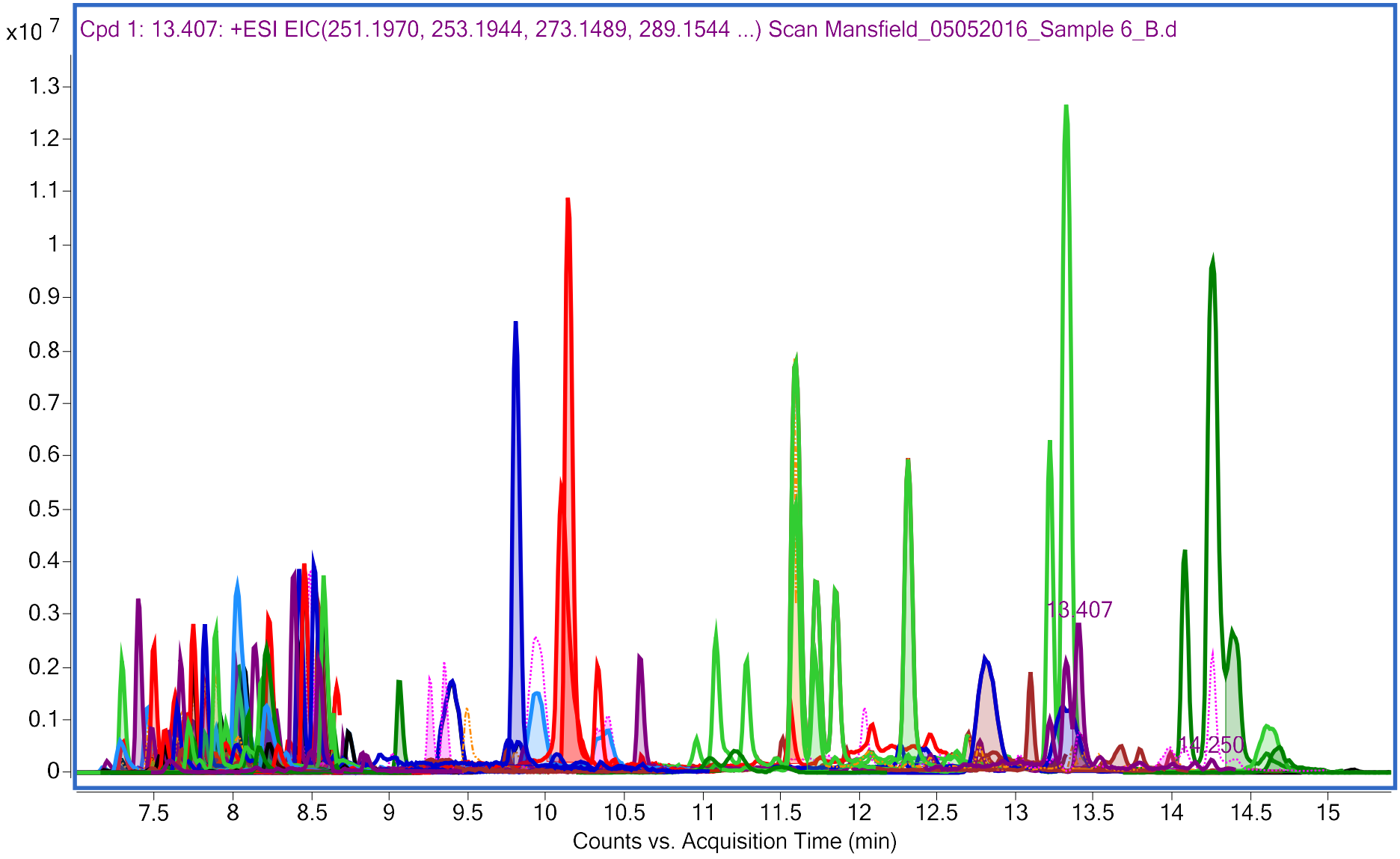
PCA Scores Plot



Tukeys HSD 746 Entities Location 6 vs Controls



115 Compounds in Wastewater that are absent upstream



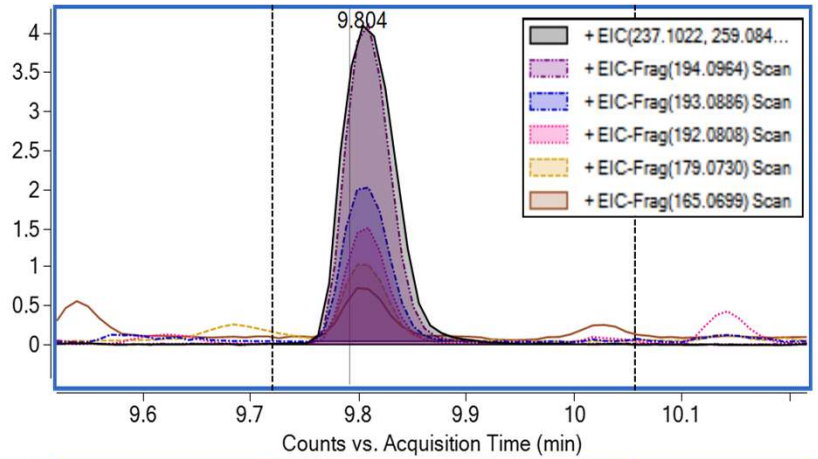
Database Search of Location 6 Only Entity List (115)

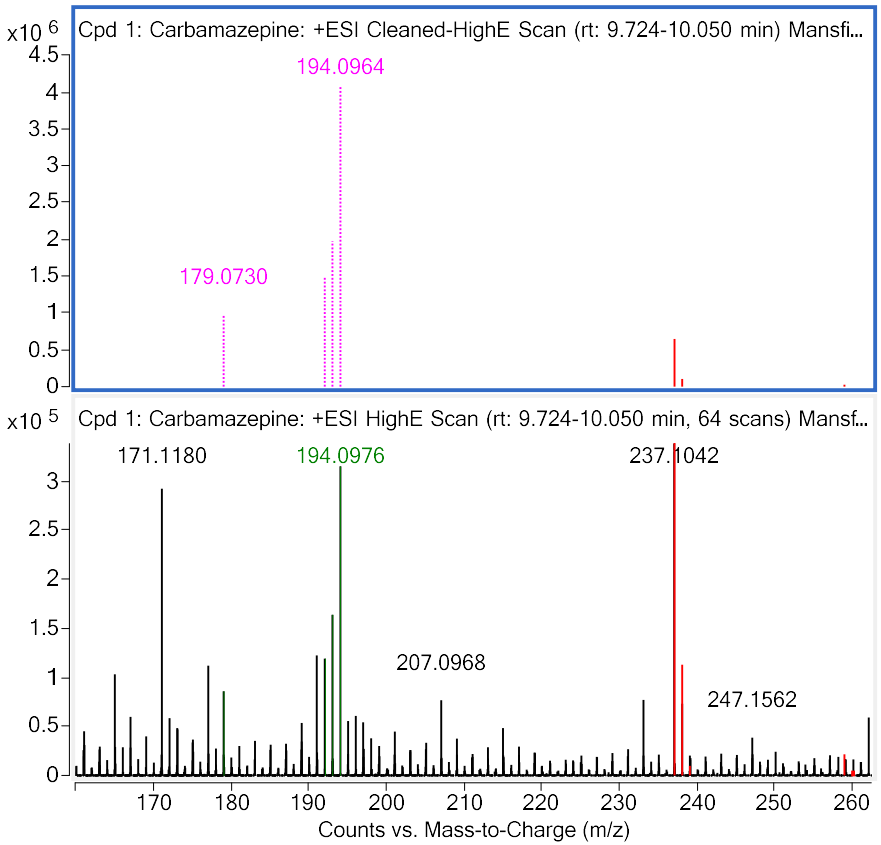
Cpd	Label	Name	Formula	Score	Mass	RT
38	Cpd 38: Valethamat; C19 H32 N O2; 9.273	Valethamat	C19 H32 N O2	99.86	306.2436	9.273
63	Cpd 63: trans-10,11-Dihydroxy-10,11-dihydroca...	trans-10,11-Dihydroxy-10,11-dihydro...	C15 H14 N2 O3	53.99	270.0956	8.167
56	Cpd 56: Sulmepride; C14 H21 N3 O4 S; 7.749	Sulmepride	C14 H21 N3 O4 S	87.87	327.1231	7.749
66	Cpd 66: Pyridarone; C13 H9 N O; 10.117	Pyridarone	C13 H9 N O	97.72	195.0693	10.117
78	Cpd 78: Pipebuzone; C25 H32 N4 O2; 7.888	Pipebuzone	C25 H32 N4 O2	72.96	420.2559	7.888
65	Cpd 65: Oxcarbazepine; C15 H12 N2 O2; 9.000	Oxcarbazepine	C15 H12 N2 O2	65.54	252.0848	9
26	Cpd 26: Irbesartan; C25 H28 N6 O; 10.137	Irbesartan	C25 H28 N6 O	99.18	428.2329	10.137
61	Cpd 61: Fenretinide; C26 H33 N O2; 7.766	Fenretinide	C26 H33 N O2	9.86	391.2311	7.766
23	Cpd 23: Dehydroepiandrosterone; C19 H28 O2; 13.367					
113	Cpd 113: Carbamazepine; C15 H12 N2 O; 9.810					
34	Cpd 34: Cannogenin; C23 H32 O5; 14.660					
43	Cpd 43: Benderizine; C28 H34 N2 O2; 8.014	Benderizine	C28 H34 N2 O2	68.19	430.2665	8.014
22	Cpd 22: 3-(4-methylbenzylidene)-Camphor; C1...	3-(4-methylbenzylidene)-Camphor	C18 H22 O	58.54	254.1662	14.274
15	Cpd 15: 17 a-Estradiol; C18 H24 O2; 14.100	17 a-Estradiol	C18 H24 O2	96.94	272.1783	14.1
17	Cpd 17: 17 a-Estradiol; C18 H24 O2; 12.390	17 a-Estradiol	C18 H24 O2	85.62	272.1785	12.39
1	Cpd 1: C11 H24 N2 O4; 11.602		C11 H24 N2 O4	95.26	248.1733	11.602
2	Cpd 2: C32 H17 N2; 8.603		C32 H17 N2	93.34	429.1394	8.603
3	Cpd 3: C21 H31 N O2 S2; 9.640		C21 H31 N O2 S2	87.13	393.1802	9.64
4	Cpd 4: C18 H20 N; 13.417		C18 H20 N	83.16	250.1592	13.417
5	Cpd 5: C16 H24 O2; 12.329		C16 H24 O2	96.9	248.1786	12.329
6	Cpd 6: C10 H24 N3 O5; 12.635		C10 H24 N3 O5	83.74	266.1713	12.635
7	Cpd 7: C9 H24 N4 O2 S; 12.036		C9 H24 N4 O2 S	72.88	252.1616	12.036
8	Cpd 8: C14 H38 N4 O3 P5; 9.639		C14 H38 N4 O3 P5	87.1	465.163	9.639

Identification of Unknowns- Data Independent Analysis

All Ions MS/MS

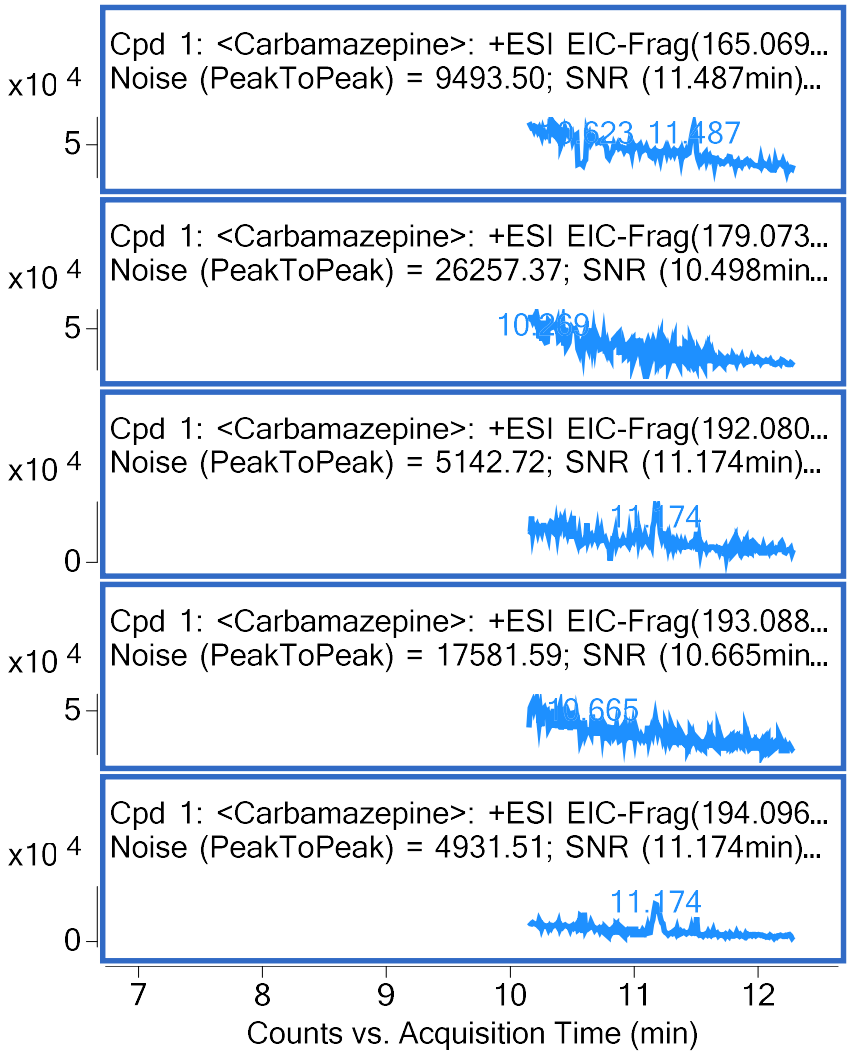
Coelution Score	CE	Flags(FIs)	FV	Height	m/z
98.8	10	Qualified		4092627	194.0964
98.6	40	Qualified		1973776.7	193.0886
97.1	40	Qualified		1485877.2	192.0808
96.4	40	Qualified		972295.9	179.073
89.6		Low coelution score		633932.9	165.0699



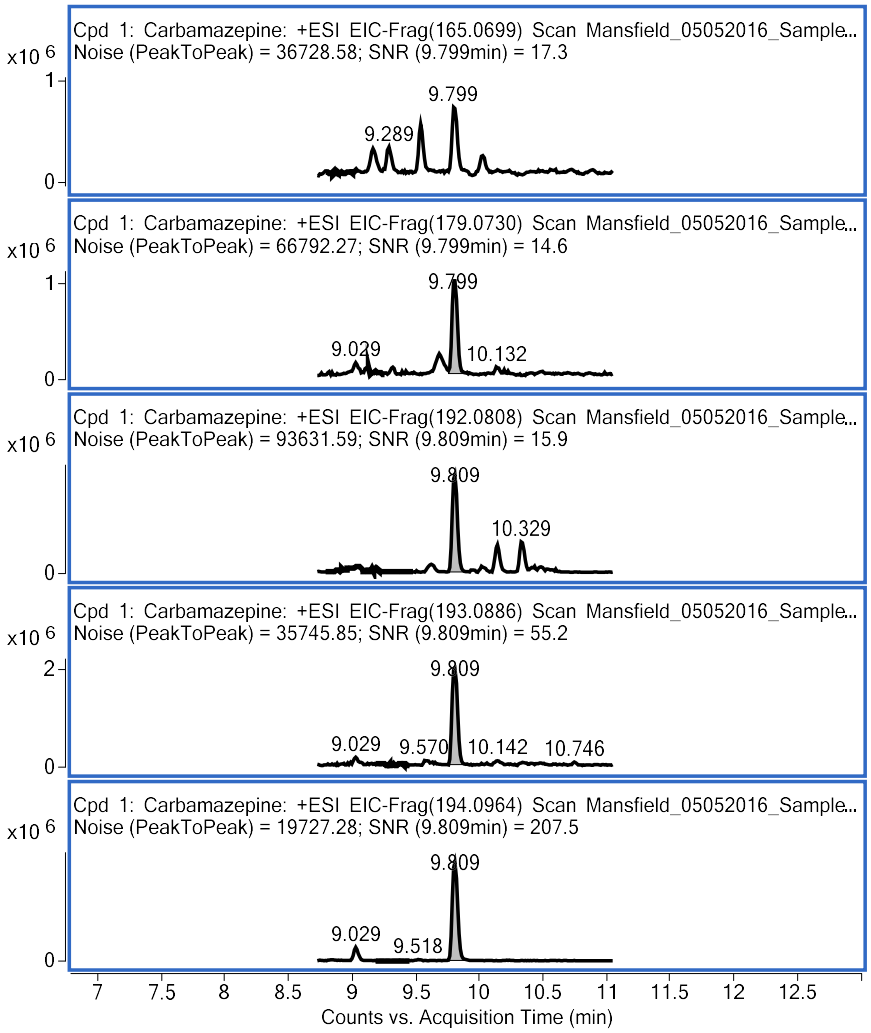


Carbamazepine

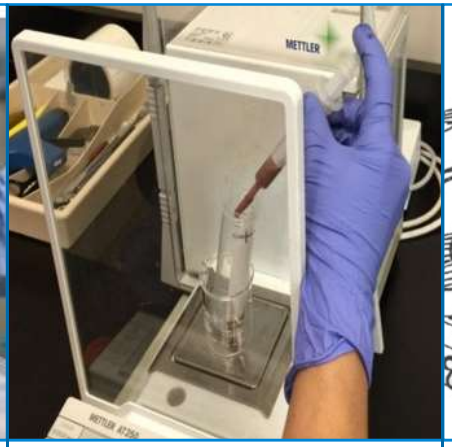
Sample Location 5



Sample Location 6



Pain Points for Analysis



Compounds to monitor

Sample Preparation

Standard Preparation

Data Analysis

Analysis of Water Contaminants
Summary

- The current LC-QTOF MS systems can offer rapid screening of several hundred emerging compounds in real water samples
- Online Automated SPE allows users to analyze samples rapidly and with very little water sample while maintaining sensitivity
- All Ions MS/MS workflow allows for additional verification tools in suspect screening with fragment confirmation and retention time through personal compound database and libraries (PCDLs)
- Several contaminants are detected in water; statistical analysis to choose SIGNIFICANT ones are essential

Agilent Technologies

For more information please visit:

www.agilent.com/en-us/solutions/environmental

Speaker contact: tarun.anumol@agilent.com