Accurate Mass Library for PFAS Analysis in Environmental Samples Using High Resolution GC/Q-TOF

National Environmental Monitoring Conference 2023

Minneapolis, MN

Tarun Anumol[1], Sofia Nieto[1], Matthew Giardina[1], Luann Wong[2], Gabrielle Black[2] , Thomas Young[2]

[1] Agilent Technologies Inc.

[2] University of California - Davis

Agilent

Trusted Answers

DE27994792

Background

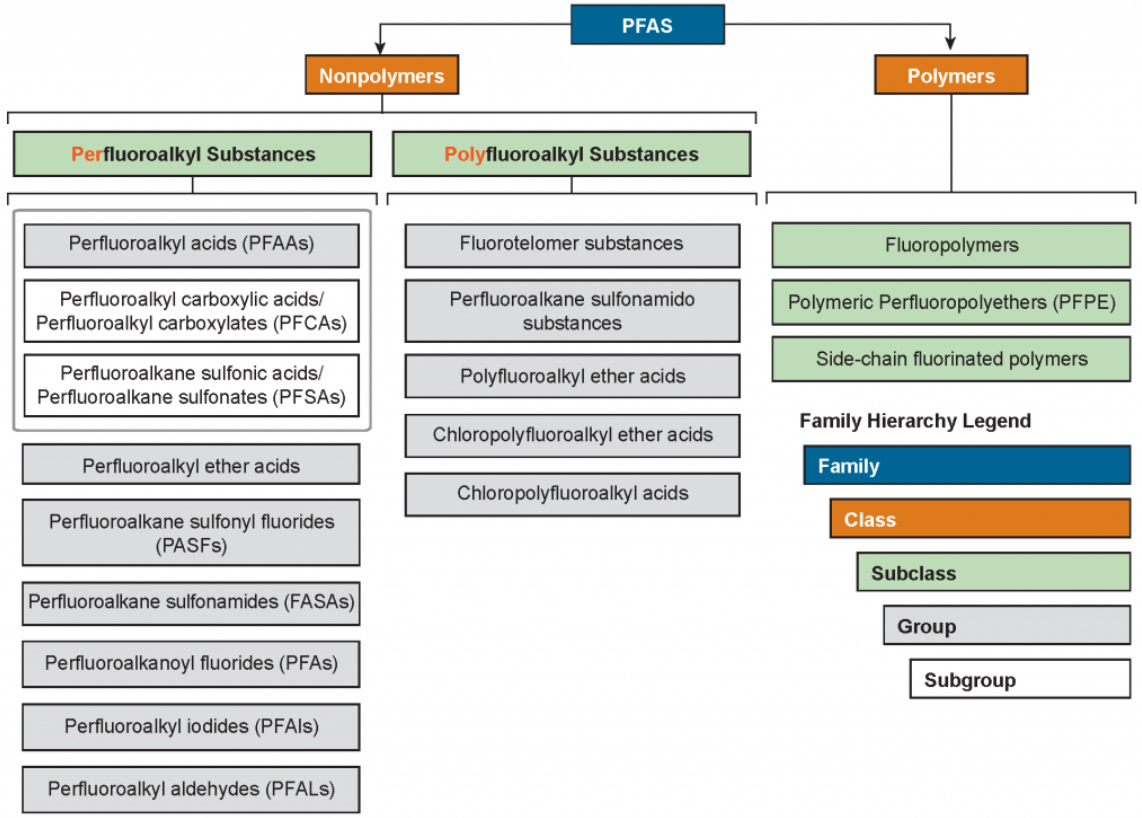
Per- and polyfluoroalkyl substances (PFAS) are emerging contaminants that are found in water, air, soil as well as wildlife

There are currently thought to be over 6,000 PFAS that have been commercially produced

A subset of PFAS that have been detected in the environment can be volatile or semi-volatile

A variety of analytical techniques are necessary for their detection

GC/MS is typically used for detecting volatile and non-polar PFAS compounds

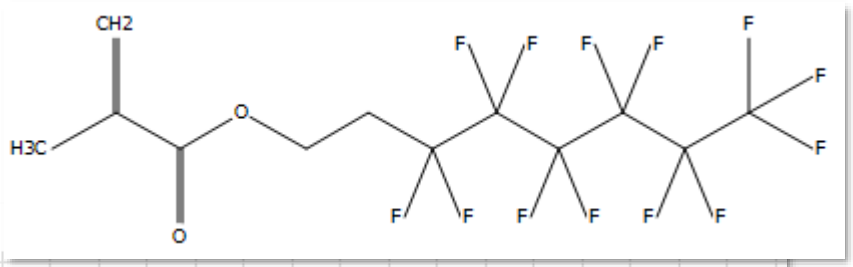


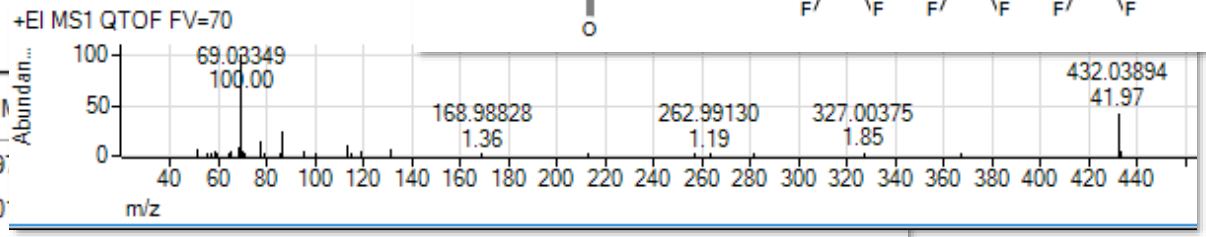
PFAS Family & Classes

(ITRC; https://pfas-1.itrcweb.org/2-2-chemistry-terminology-and-acronyms/)

Accurate Mass GC/MS Libraries

- ❖Allow for flexibility of workflows (targeted and non-targeted)
- ❖Improve confidence in identification due to accurate mass
  - Time-efficient: less review required
  - Decrease false positive rate





Name	Formula	M			
2,2-Difluoroethyl triflate	C3H3F5O3S	213.9			
Flurotyl	C4H4F6O	182.0			
4H-Perfluorobutanoic acid	C4H2F6O2	195.9959	14.354	679-12-9	DTXSID50892417
PFUnDA / Perfluoroundecanoic acid (PFUnA)	C11HF21O2	563.96412	6.124	2058-94-8	全氟十一烷酸; Perfluoro-n-undeca...
Perfluoropentanamide	C5H3F8NO	245.00869	37.26	355-81-7	DTXSID70366226
6:2 Fluorotelomer methacrylate	C12H9F13O2	432.0395	36.783	2144-53-8	2-(Perfluorohexyl)ethyl methacrylate;...
8:2 Fluorotelomer sulfonic acid	C10H5F17O3S	527.96879	37.44	39108-34-4	DTXSID00192353
N-Methyl-N-(2-hydroxyethyl)perfluorooctanesulfon...	C11H8F17NO3S	556.99534	45.813	24448-09-7	DTXSID7027831
11:1 Fluorotelomer alcohol	C12H3F23O	599.98166	36.678	423-65-4	DTXSID80375107

Workflows for the Accurate Mass PCDL

Acquire full-spectrum data

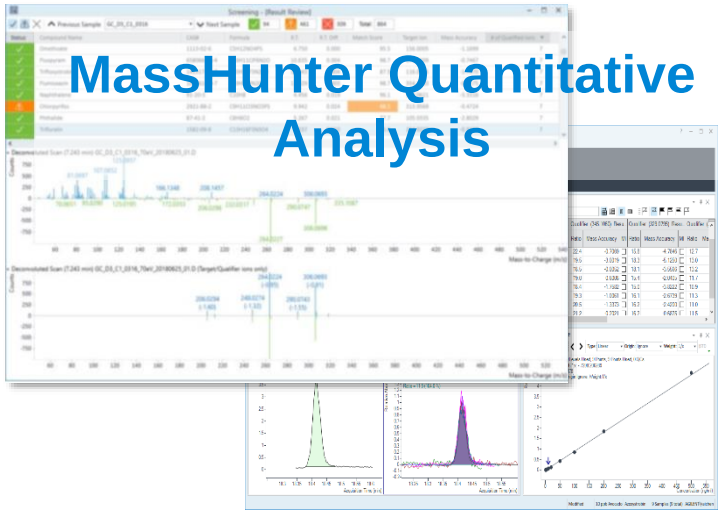
Targeted Method

Peak Picking

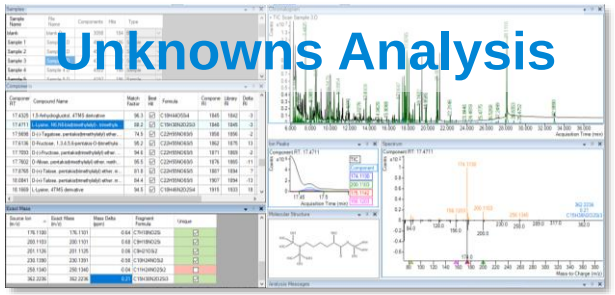
Targeted Screening/ Quantitation

Non-Targeted Screening

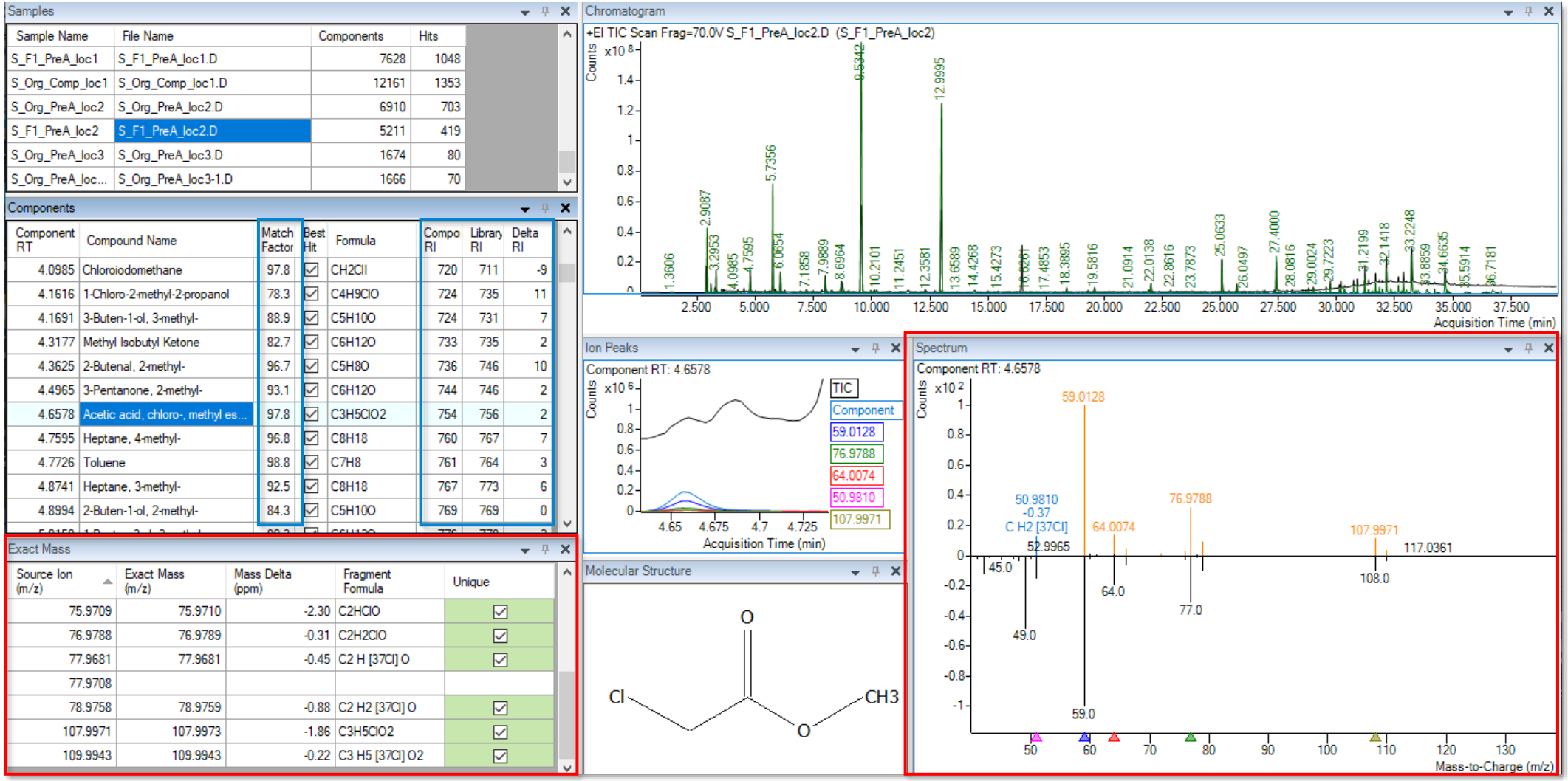
MassHunter Quantitative Analysis



Unknowns Analysis



Non-Targeted Screening Workflow



Agilent

Target/Suspect Screening and Quantitation

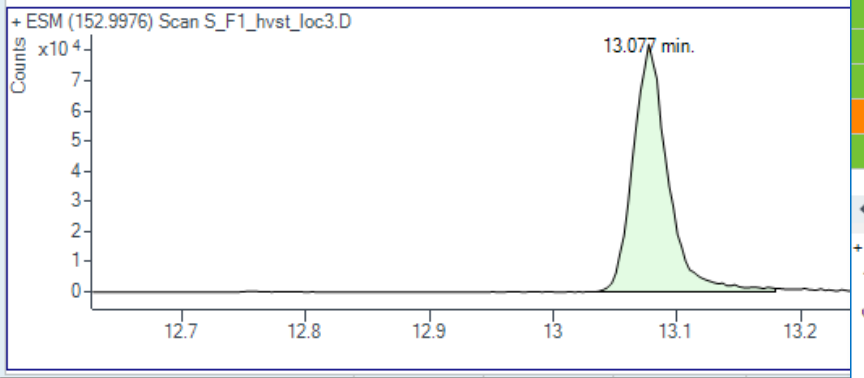
Detailed Results table

Batch Table

Sample Type: <All> Compound: Chlorbufam

Compound Method	S_F1_hvst_loc3			Qualifier 1 Results			
Name	RT	Final Conc.	S/N	Coelution Score	Mass Accuracy	S/N	Coelution Score
4-Aminobiphenyl	19.014		2.18	0.0	-11.6185	3.07	
Dimethipin							
Monolinuron							
Chlorbufam	13.077		328.38				
Swep (MCC)	16.560		1857.67				
Carbofuran	15.459		8.28				

Compound Information

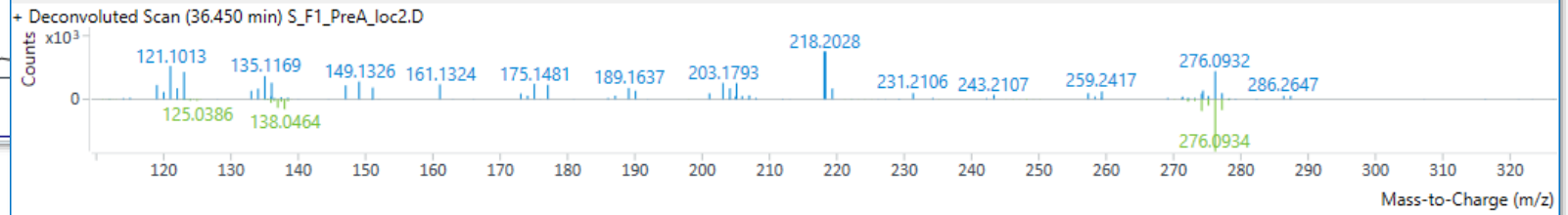


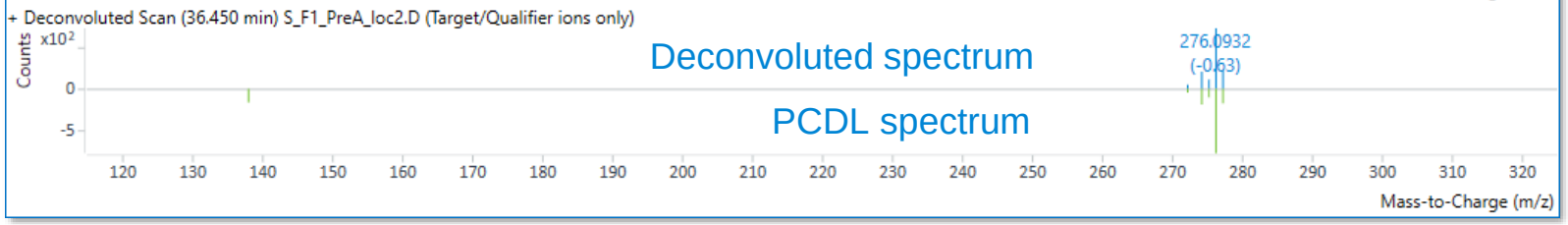
Screener Summary Window

Screening - [Result Review]

Targets Suspects Previous Sample S_F1_PreA_loc2 Next Sample 28 58 1044 Total: 1130

Status	Promoted	Compound Name	CAS#	Formula	R.T.	R.T. Diff.	Fin...	Match Score	Target Ion	Mass Accur...	# of Verified I...
✓	☐	Benzo[e]pyrene	192-97-2	C20H12	33.484	0.125		95.5	252.0934	0.6061	3
✓	☐	Benzo[a]pyrene	50-32-8	C20H12	33.484	0.306		94.2	252.0934	0.6061	2
✓	☐	Perylene	198-55-0	C20H12	33.484	0.649		95.4	252.0934	0.6061	3
✓	☐	DNP / Dinonyl phthalate	84-76-4	C26H42O4	31.374	3.391		88.4	149.0233	2.0384	3
✓	☐	Indeno[1,2,3-cd]pyrene	193-39-5	C22H12	36.443	1.461		90.2	276.0934	-0.6308	6
⚠	☐	Imibenconazole	86598-92-7	C17H13Cl3N4S	28.986	9.028		24.5	125.0153	-1.9246	2
✓	☐	Benzo[ghi]perylene	191-24-2	C22H12	36.443	2.285		90.8	276.0934	-0.6308	6



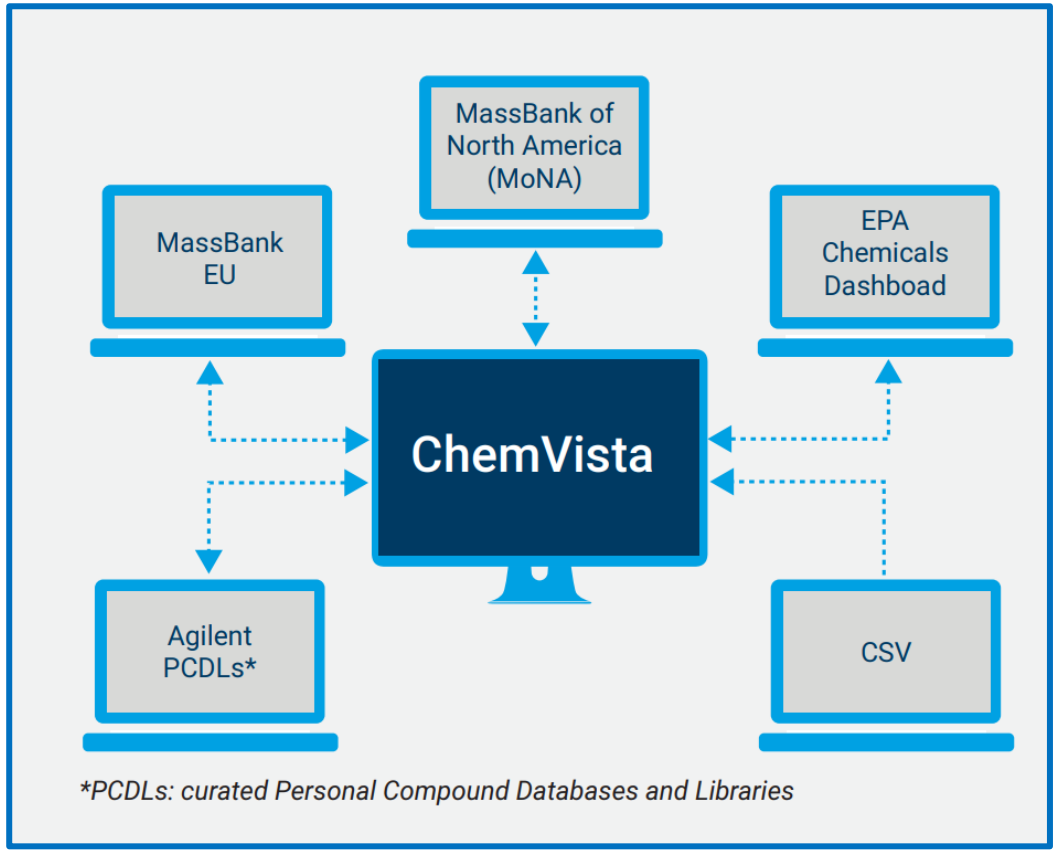


Agilent

ChemVista Library Manager

New software for managing spectra, compounds, and RTs

- Provides access to multiple public databases (import/export, export without duplicates)
- Organize, manage, edit or create spectra
- Cheminformatics underpinning for structure generation and organizational focus
- Compound centric structure allows multiple spectra, RT and RI representing different analytical conditions
- Easily generated lists cater to multiple application workflows
- Facilitate identification workflows within MassHunter data analysis applications and beyond

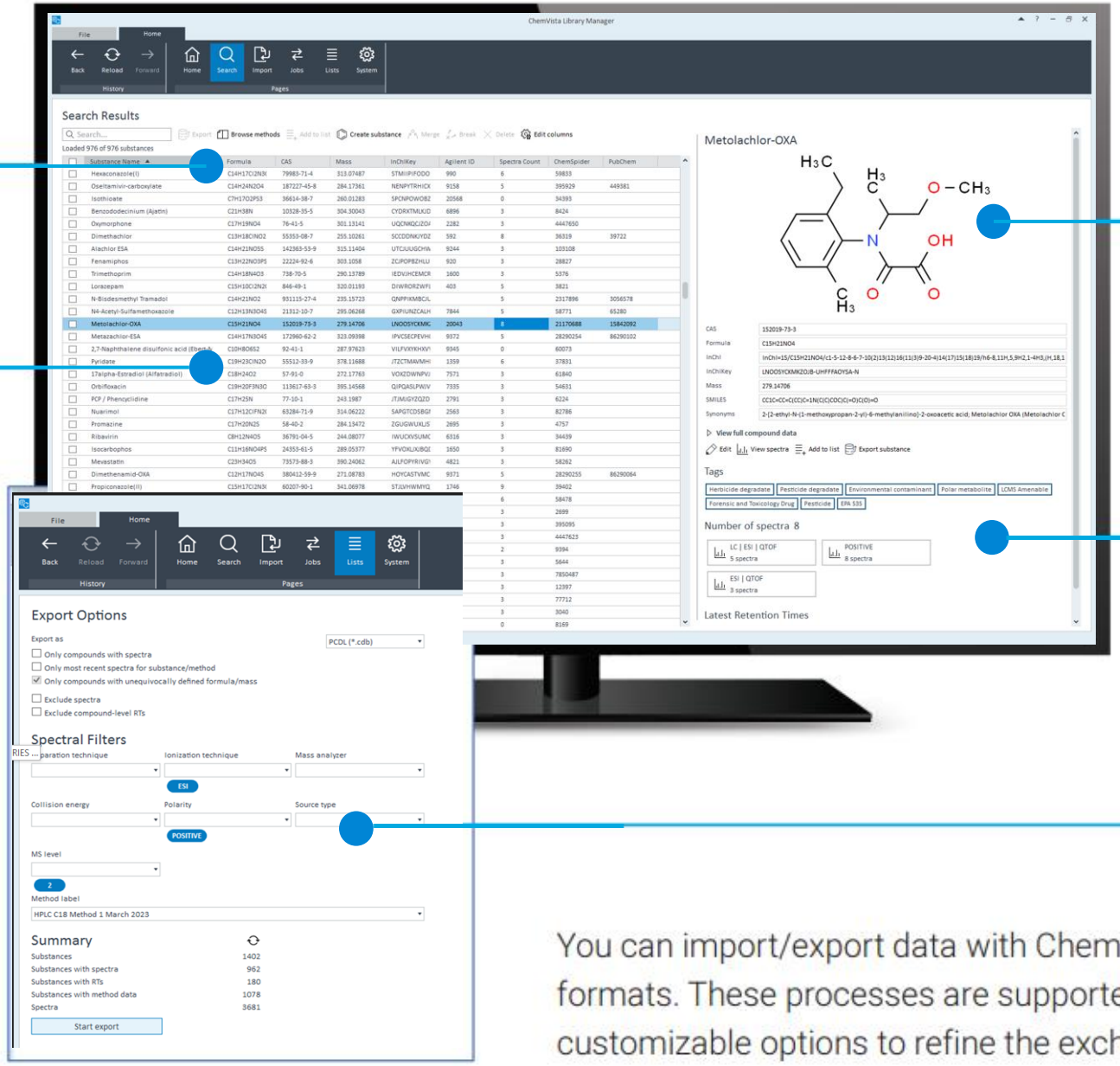


PCDL, SDF, .txt, and .csv file formats

Workflows Center Around Lists

Workflows center around lists associated with a specific analysis.

Lists serve as organizational tools, allowing a compound to exist in multiple lists with multiple spectra.



Enhanced chem informatics generate structures and identifiers, eliminating duplicates and supporting downstream workflows.

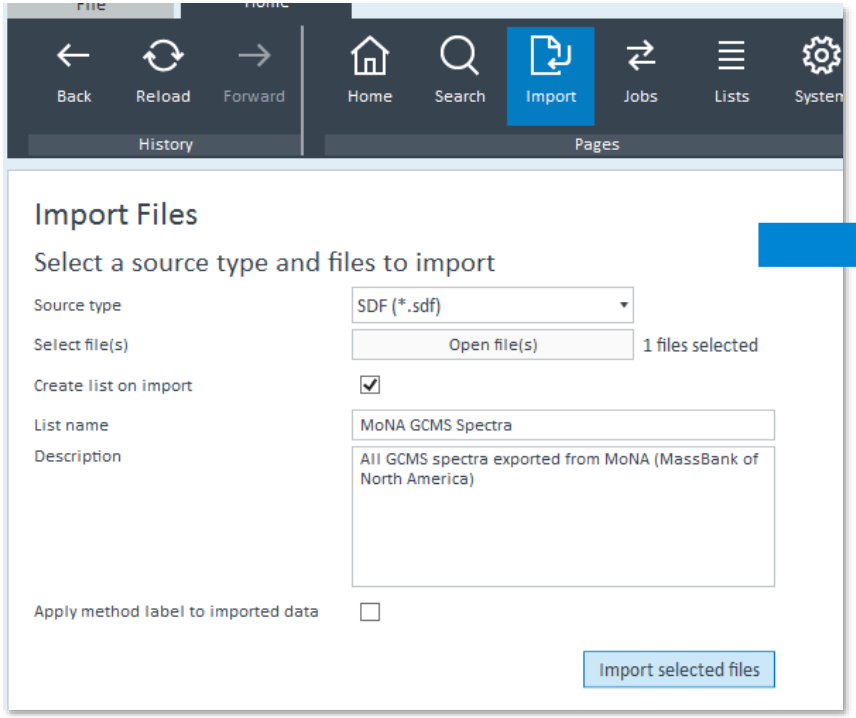
Automated chemical class tags are assigned from manually curated PCDLs.

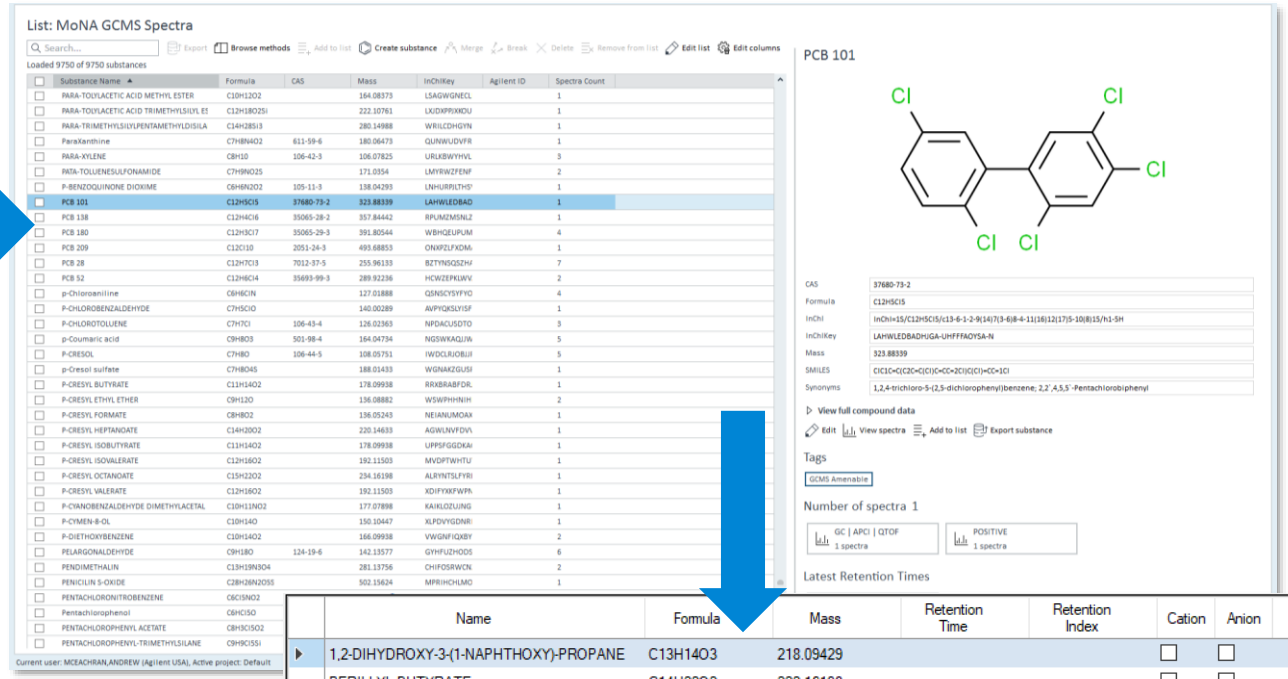
You can import/export data with ChemVista in multiple file formats. These processes are supported with filters and customizable options to refine the exchanged information.

Agilent

Using ChemVista to Enhance Identification Workflows

Import GCMS spectra from MassBank of North America (MoNA)





Export to PCDL for MassHunter Data Analysis Workflows

Name	Formula	Mass	Retention Time	Retention Index	Cation	Anion	CAS	ChemSpider
1,2-DIHYDROXY-3-(1-NAPHTHOXY)-PROPANE	C13H14O3	218.09429			☐	☐		
PERILLYL BUTYRATE	C14H22O2	222.16198			☐	☐		
Sebacic acid	C10H18O4	202.12051			☐	☐	111-20-6	5004
Galactitol	C6H14O6	182.07904			☐	☐	608-66-2	11357
Dihydroxyacetone	C3H6O3	90.03169			☐	☐	96-26-4	650
1,5-DINITRONAPHTHALENE	C10H6N2O4	218.03276			☐	☐	605-71-0	
DL-Ethionine	C6H13NO2S	163.0667			☐	☐	67-21-0	5970
2,5-DIMETHYLBENZENAMINE	C8H11N	121.08915			☐	☐		
damascenone (e-beta)	C13H18O	190.13577			☐	☐		
17BETA-ACETOXY-1ALPHA-HYDROXY-5ALPH...	C21H34O3	334.25079			☐	☐		
2,3-DIMETHYLBENZENAMINE	C8H11N	121.08915			☐	☐		
4-Hydroxyphenethyl alcohol	C8H10O2	138.06808			☐	☐	501-94-0	9964

Agilent

Sampling and Extractions

❖ Soil:

- Sampled from 2 fields in California
- Extracted with methylene chloride

❖ Drinking water samples:

- Collected from two different water source categories:
  - a small surface water (Weaverville)
  - a mixed surface and ground water (Irvine)

- Extracted on a multi-mode SPE (HLB, WAX, WCS, Isoelut ENV)
- Eluted with 5% MTBE in MeOH, DCM, 0.5% NH4OH in 1:1 EtAC:MeOH, and 1.7% formic acid in 1:1 EtAC:MeOH
- The combined extracts were concentrated, solvent exchanged to EtAc and diluted 10x

Experimental Conditions

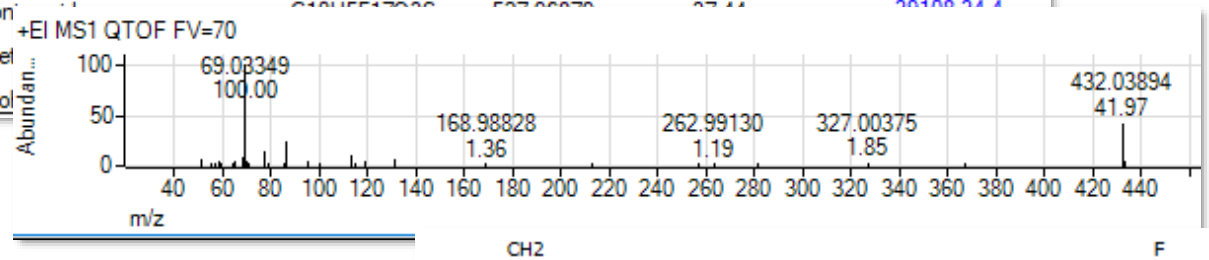
GC and MS Conditions	DB-5MS	DB-624
MS	7250 Q-TOF	
GC	7890	
Inlet	MMI, 4-mm UI liner single taper with wool	
Inlet temperature	70 °C for 0.01 min; 300 °C/min to 250 °C	
Injection volume	1 µL	
Columns	DB-5MS UI, 30 m x 0.25 mm x 0.25 µm	DB-624 UI, 30 m x 0.25 mm x 1.4 µm
Oven temperature program	35 °C for 2 min; 7 °C/min to 210 °C, 20 °C/min to 300 °C, 4 min hold	30 °C for 2 min; 3 °C/min to 75 °C, 2 °C/min to 110 °C, 10 °C/min to 210 °C, 20 °C/min to 240 °C, 2 min hold
Column flow	1.2 mL/min constant flow	1 mL/min constant flow
Carrier gas	Helium	
Transfer line temperature	250 °C	
Quadrupole temperature	150 °C	
Source temperature	200 °C	
Electron energy	70 eV	
Emission current	Variable by time segment, 0.01 to 5 µA	
Spectral acquisition rate	5 Hz	
Mass range (Tune)	50 to 1200 m/z	

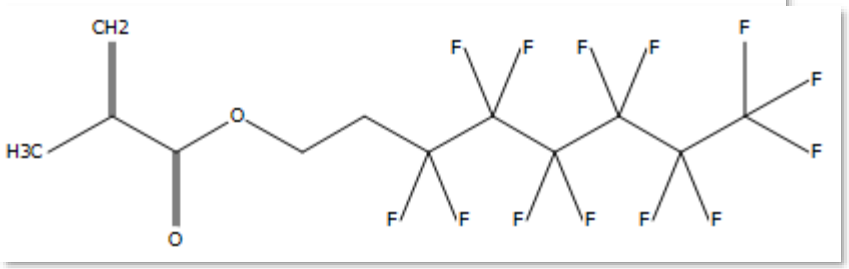
7250 GC/Q-TOF

Accurate Mass PFAS Library for GC/Q-TOF

- Contains high resolution accurate mass spectra of over a hundred PFAS compounds (~140)
- Expert curated and converted to theoretical m/z
- Retention Time
- Molecular structures
- CAS and other identifiers

Name	Formula	Mass	Retention Time	CAS
2,2-Difluoroethyl triflate	C3H3F5O3S	213.97231	12.25	74427-22-8
Flurotyl	C4H4F6O	182.01663	3.74	333-36-8
4H-Perfluorobutanoic acid	C4H2F6O2	195.9959	14.354	679-12-9
PFUnDA / Perfluoroundecanoic acid (PFUnA)	C11HF21O2	563.96412	6.124	2058-94-8
Perfluoropentanamide	C5H3F8NO	245.00869	37.26	355-81-7
6:2 Fluorotelomer methacrylate	C12H9F13O2	432.0395	36.783	2144-53-8
8:2 Fluorotelomer sulfon				
N-Methyl-N-(2-hydroxyet				
11:1 Fluorotelomer alcol				

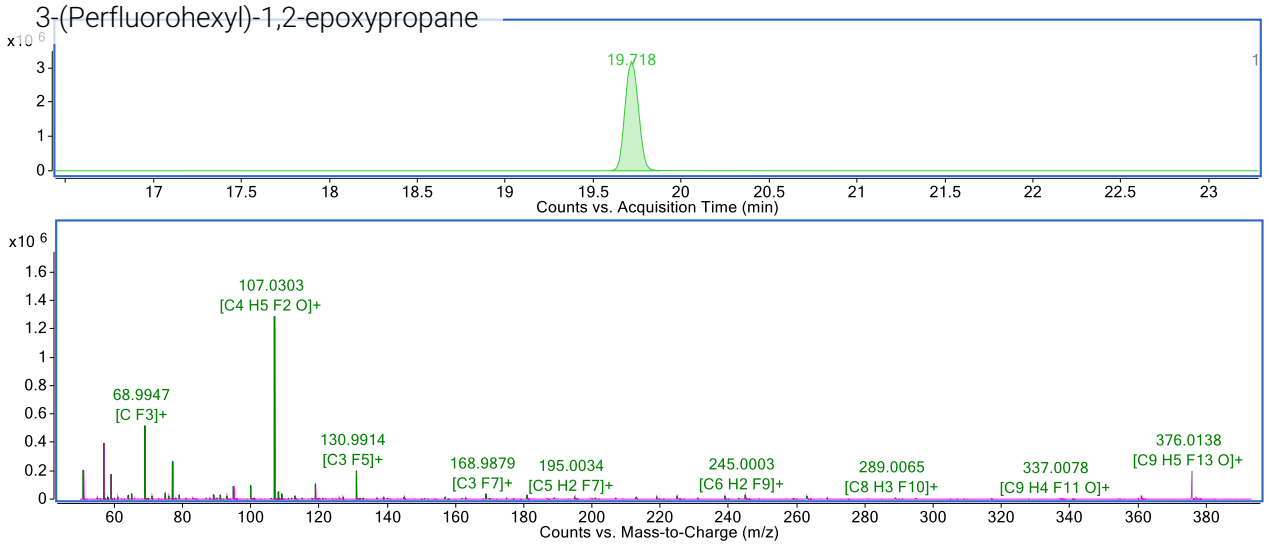




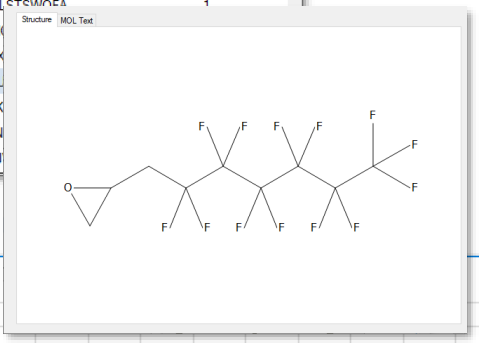
Agilent

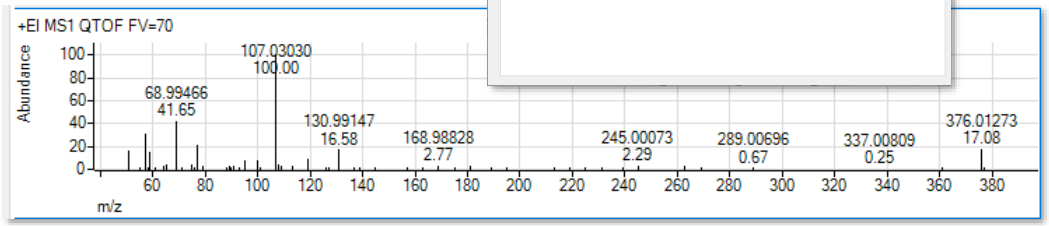
Creation of the Accurate Mass PCDL

- Automated fragment formula annotation based on accurate mass and isotope ratios
- Conversion to theoretical m/z
- Noise ions are automatically removed



Name	Formula	Mass	Retention Time	CAS	IUPAC	SMILES	InChI Key	InChI	NumSpectra
Perfluoro-3,6,9-trioxatridecanoic acid	C10HF19O5	561.95206	18.85	330562-41-9	Difluoro(1,1,2,2-t...	OC(=O)C(F)(F)OC(...	GDQL		1
1-(Perfluorofluorooctyl)propane-2,3-diol 2	C11H7F17O2	494.01746	18.89	94159-84-9	4,4,5,5,6,6,7,7,8,...	OCC(O)CC(F)(F)C(...	CGRI		
3H-Perfluoro-2,2,4,4-tetrahydroxypentane	C5H5F7O4	262.00761	19.54	77953-71-0	1,1,1,3,5,5,5-Hep...	OC(O)(C(F)C(O)(O...	NZCX		
3-(Perfluorohexyl)-1,2-epoxypropane	C9H5F13O	376.01328	19.71	38565-52-5	2-(2,2,3,3,4,4,5,5,...	FC(F)(F)C(F)(F)C(F...	KGYU		
3-(Perfluoropropyl)propanol	C6H7F7O	228.03851	20.206	679-02-7	4,4,5,5,6,6,6-Hep...	OCCCC(F)(F)C(F)(...	VACK		
6:1 Fluorotelomer alcohol	C7H3F13O	349.99763	20.56	375-82-6	2,2,3,3,4,4,5,5,6,...	OCC(F)(F)C(F)(F)C...	STLN		
1-Iodo-1H,1H,2H,2H-perfluoroheptane	C7H4F11I	423.9182	21.35	1682-31-1	1,1,1,2,2,3,3,4,4,...	FC(F)(F)C(F)(F)C(F...	KEHJ		

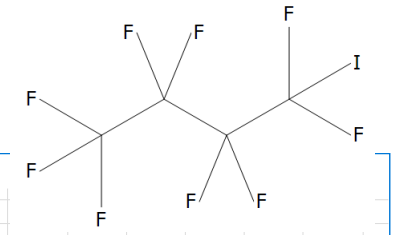


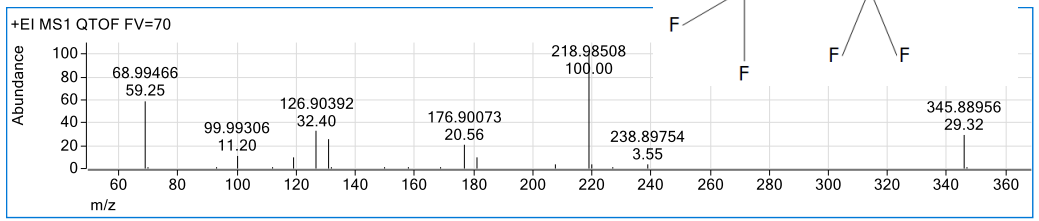


Agilent

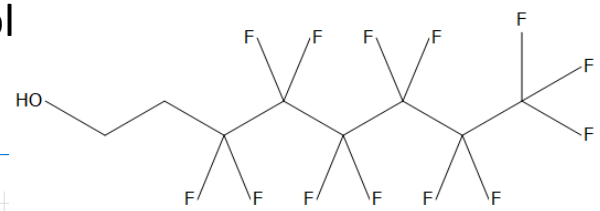
PFAS Classes in the PCDL

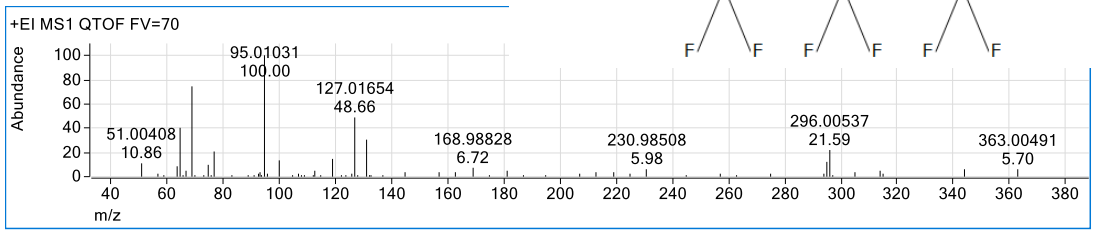
Nonafluoro-1-iodobutane (PFBI)



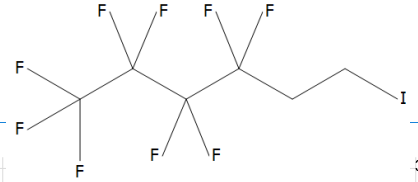


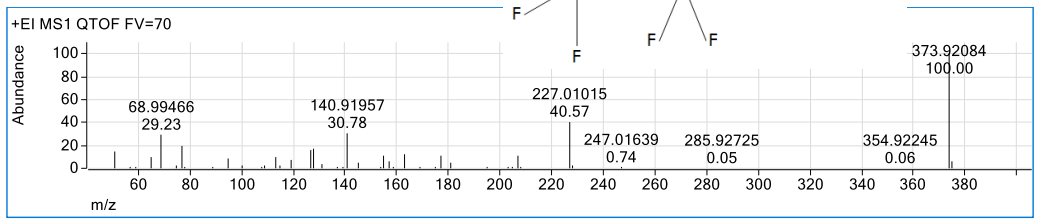
6:2 Fluorotelomer alcohol (6:2 FTOH)



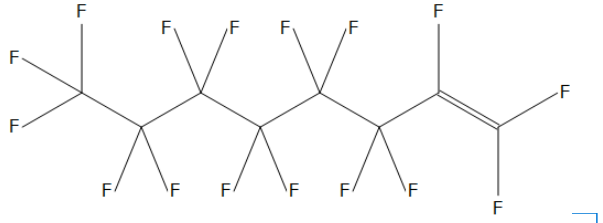


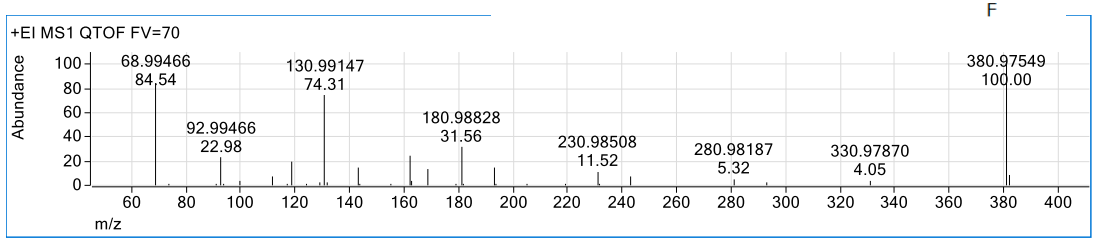
1,1,1,2,2,3,3,4,4-Nonafluoro-6-iodohexane (6:2 FTI)





Perfluorooct-1-ene

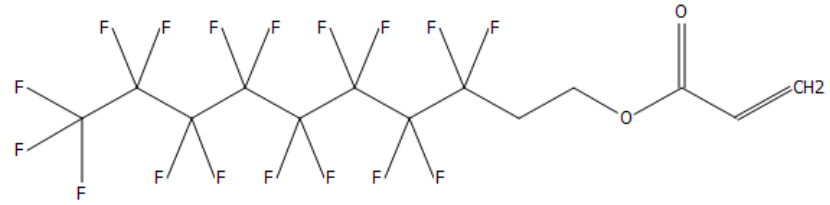


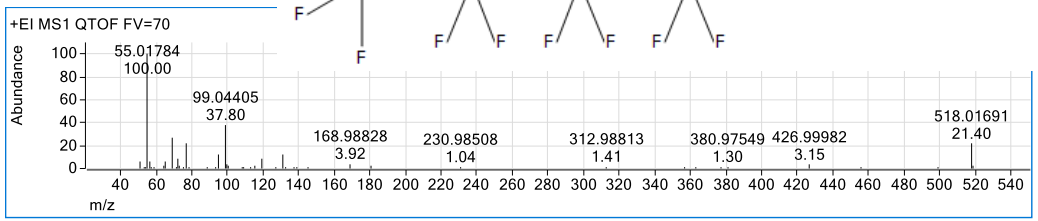


Agilent

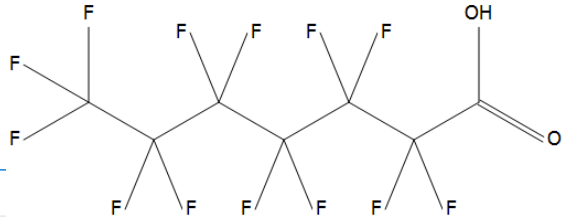
PFAS Classes in the PCDL

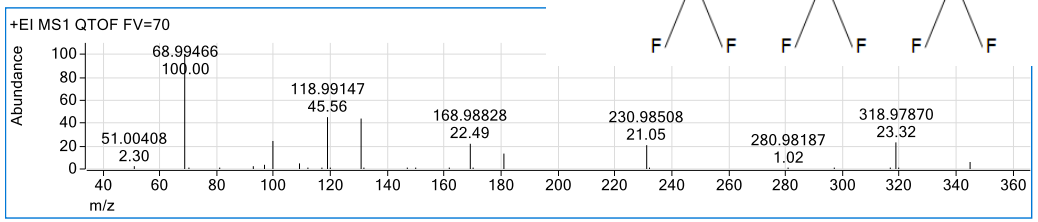
8:2 Fluorotelomer acrylate (8:2 FTAC)



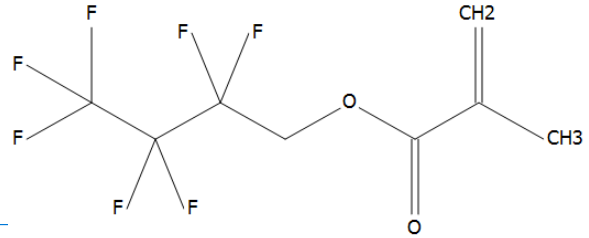


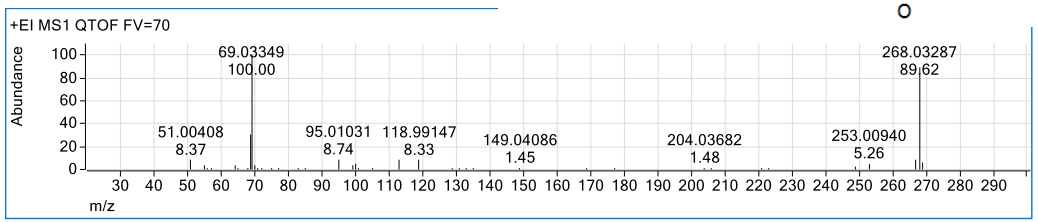
Perfluoroheptanoic acid (PFHpA)



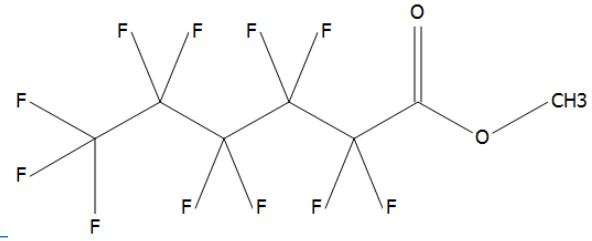


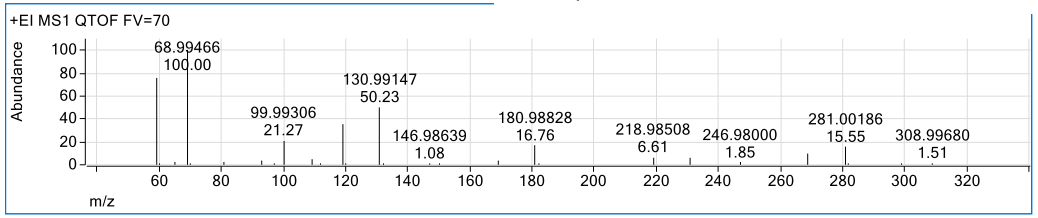
2,2,3,3,4,4,4-Heptafluorobutyl methacrylate (3:1 FTMAC)





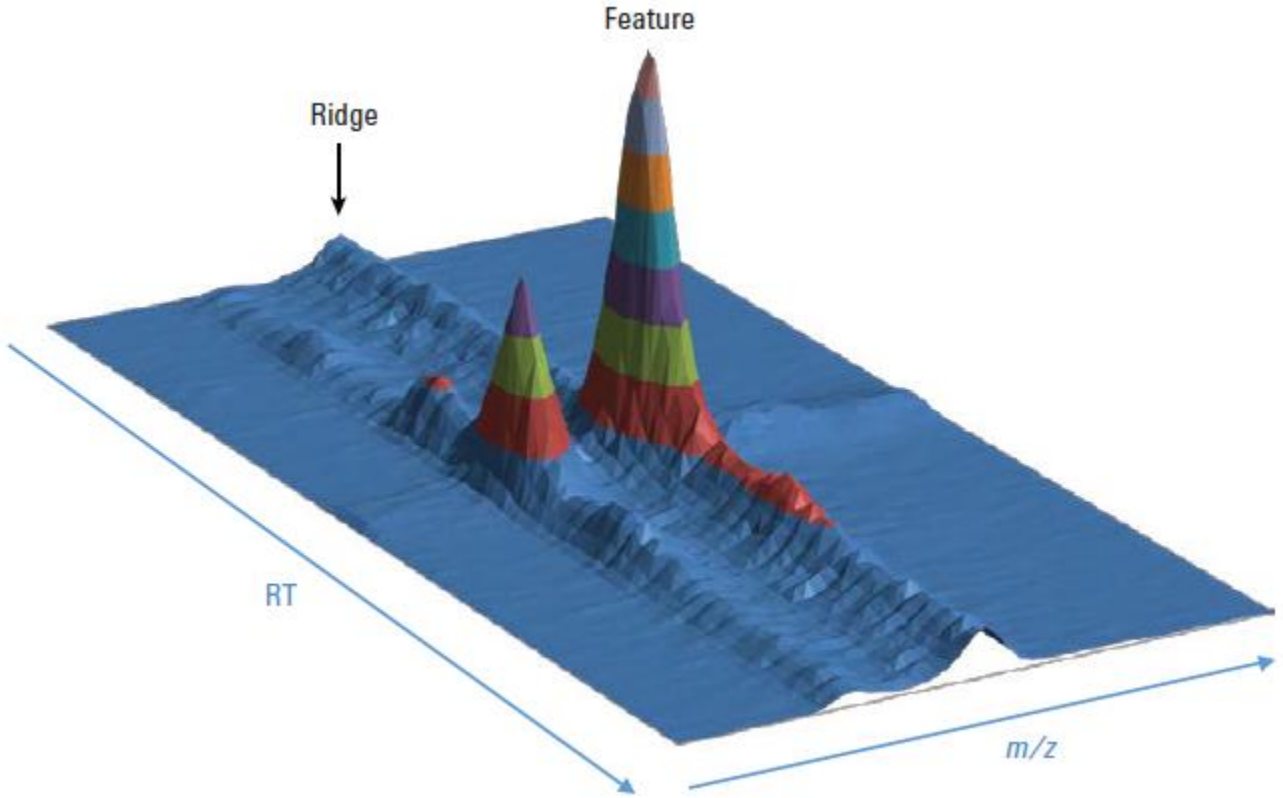
Methyl perfluorohexanoate





Agilent

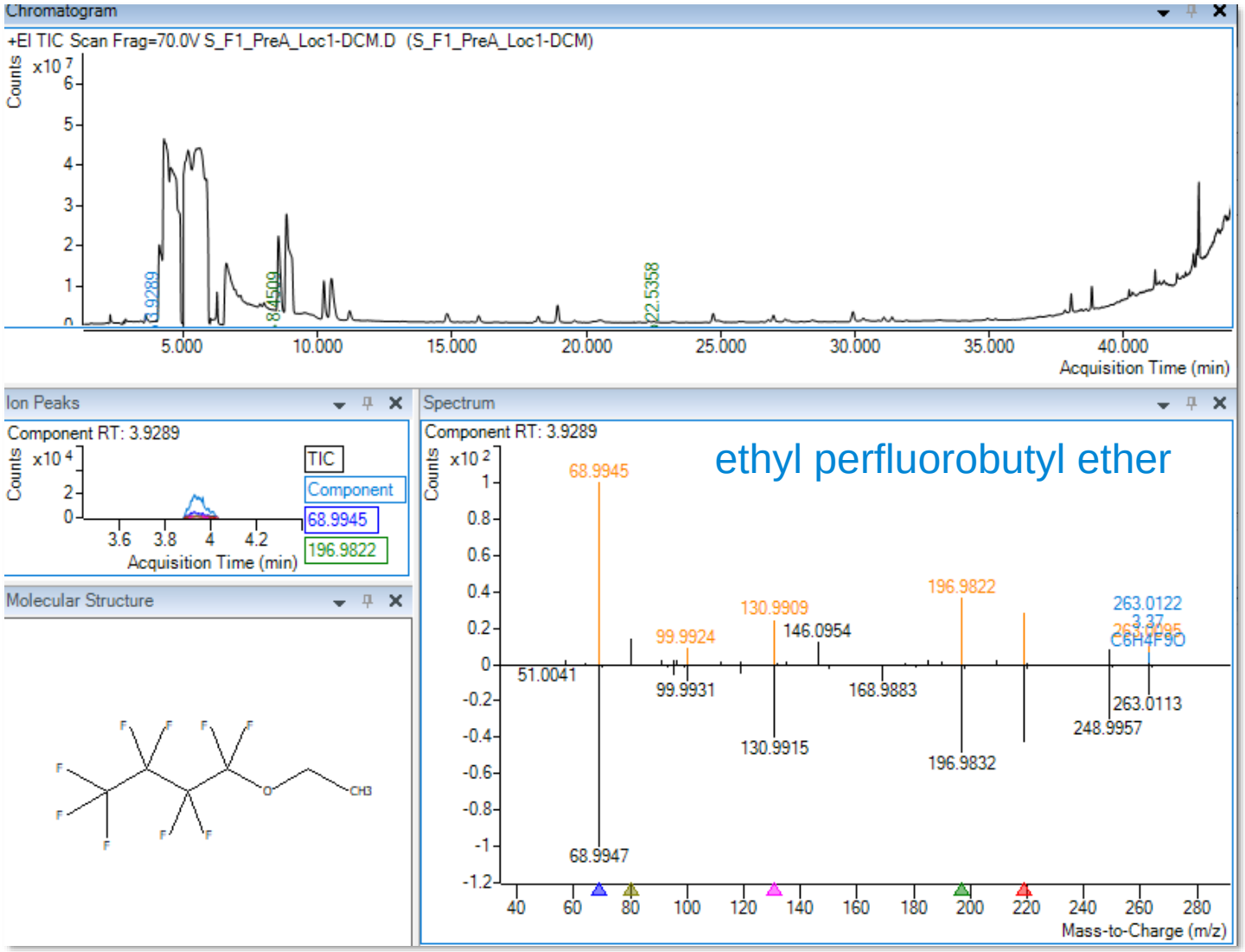
SureMass Deconvolution and Library Search



SureMass signal processing

Examples of PFAS Identified in Soil and Water Using the PFAS PCDL

Sample: soil extracted from Field 1



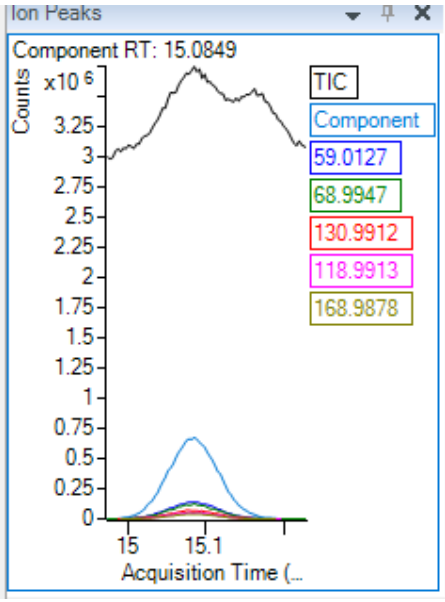
Examples of PFAS Identified in Soil and Water Using the PFAS PCDL

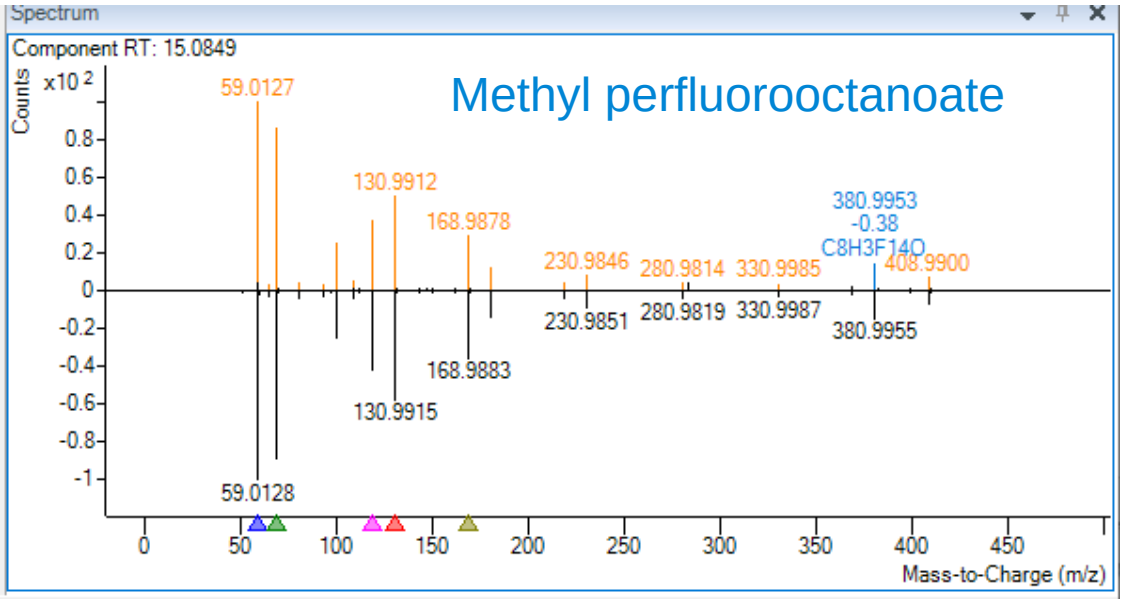
Sample: drinking water (Irvine)

Component RT	Compound Name	Match Factor	Best Hit	Formula	Delta RT
15.0849	Methyl perfluorooctanoate	97.6	☑	C9H3F15O2	-0.2599

Exact Mass

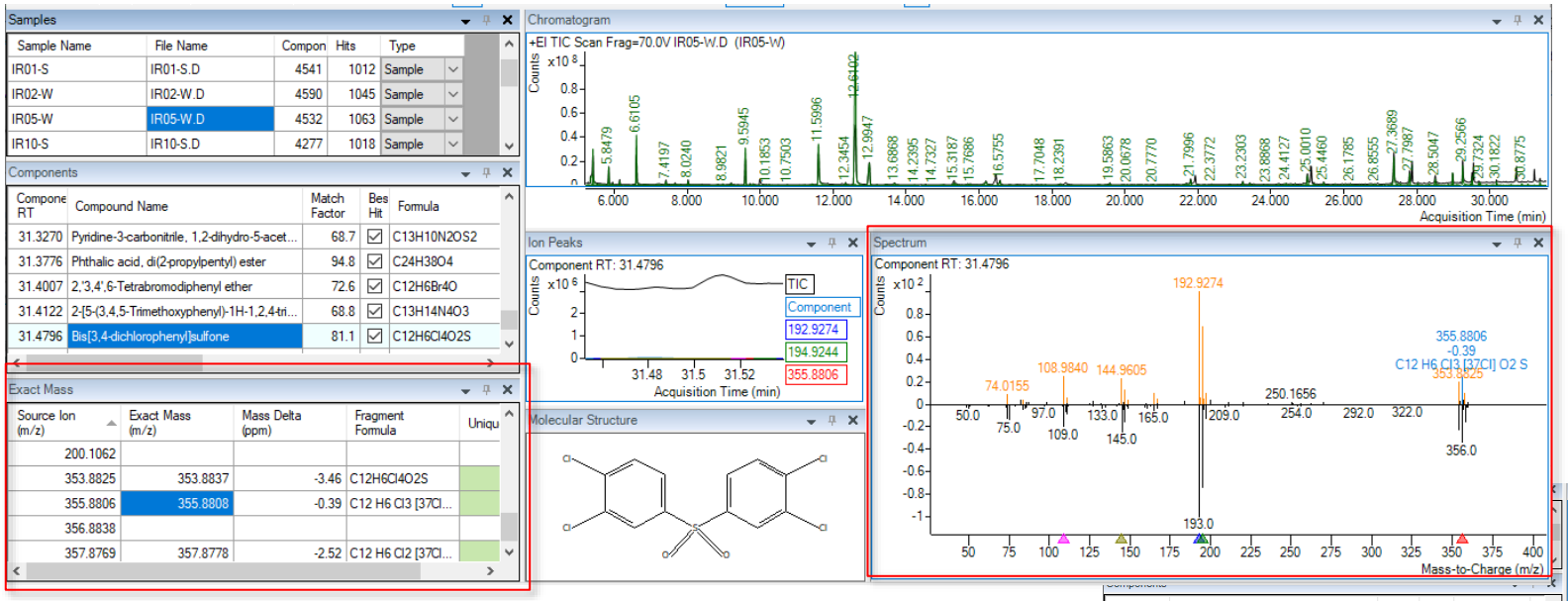
Source Ion (m/z)	Exact Mass (m/z)	Mass Delta (ppm)	Fragment Formula
230.9846	230.9851	-2.10	C5F9
280.9814	280.9819	-1.88	C6F11
281.0014	281.0019	-1.70	C6H3F10O
283.0487			
330.9985	330.9987	-0.64	C7H3F12O
380.9953	380.9955	-0.38	C8H3F14O
408.9900	408.9904	-0.99	C9H3F14O2



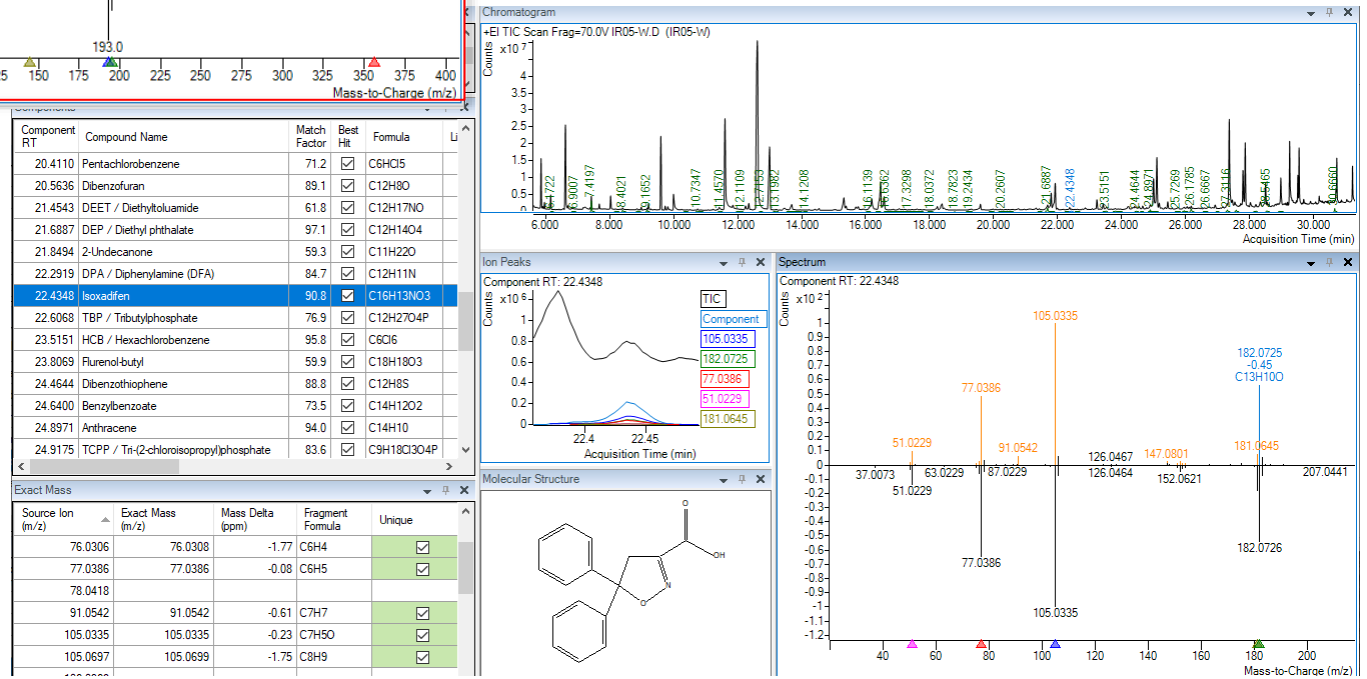


Agilent

Additional Contaminants in Drinking Water Samples



NIST20



Pesticides PCDL

Agilent

Additional Contaminants in Drinking Water Samples

Disinfection by-products:

*Bromodichloromethane
*Chloral
*Dichloroacetonitrile
*Bromoacetonitrile
*Dibromochloromethane
1,1-Dimethyl-3-chloropropanol
*Bromochloroacetonitrile
Dichloroacetic acid methyl ester
*Tribromomethane
Methyl bromo(chloro)acetate
*Dibromoacetonitrile
2,2-Dichloroacetamide

NIST20

Library Match score >75

** - known or probable carcinogens*

Additional Contaminants in Drinking Water Samples

Industrial processes:

*Tetrachloroethylene
1,2-Dichlorbenzene
Caprolactam
Phthalic anhydride
Biphenyl
Dimethyl phthalate
2,4-Di-tert-butylphenol
Dibenzofuran
Diethyl Phthalate
2-(Methylmercapto)benzothiazole
Tributyl phosphate
*Tris(2-chloroisopropyl)phosphate
Di-sec-butyl phthalate
Dibutyl phthalate
Octachlorostyrene
Drometrizole
Pyrene
*Bisphenol A
Bis(4-chlorophenyl) sulfone
2,2'-Methylene-bis-(4-methyl-6-t-butylphenol)
Phthalic acid, di(2-propylpentyl) ester
Bis[3,4-dichlorophenyl]sulfone
*Bumetrizole
*Bis(2-ethylhexyl) isophthalate
*Decachlorobiphenyl

NIST20

*2-Picoline
*Methanesulfonate-methyl
*o-Toluidine
Phenol
*2,4,5-Trimethylaniline
2-Nitrophenol
Diphenylamine

Pesticides and environmental contaminants PCDL

Library Match score >75

* - *known or probable carcinogens*

Additional Contaminants in Drinking Water Samples

PAHs and their derivatives:

*Naphthalene	9-Methylene-fluorene
2-Methylnaphthalene	3-Methylphenanthrene
Acenaphthene	2-Methylanthracene
Fluorene	Cyclopenta(def)phenanthrenone
9H-Fluoren-9-one	Fluoranthene
9H-Fluoren-9-ol	Pyrene
*Anthracene	1-Azapyrene

NIST20

Library Match score >75

* - *known or probable carcinogens*

Additional Contaminants in Drinking Water Samples

Personal care products:

Dimethyl phthalate
Diethyl Phthalate
*Benzophenone
Di-sec-butyl phthalate

p-Phenylenediamine
Acetophenone

NIST20

Library Match score >75

** - known or probable carcinogens*

Pesticides and environmental contaminants PCDL

Additional Contaminants in Drinking Water Samples

Pesticides:

Diethyltoluamide (DEET)
*Hexachlorobenzene
Cyclic octaatomic sulfur

Thanite
Benzaldehyde
Isoxadifen

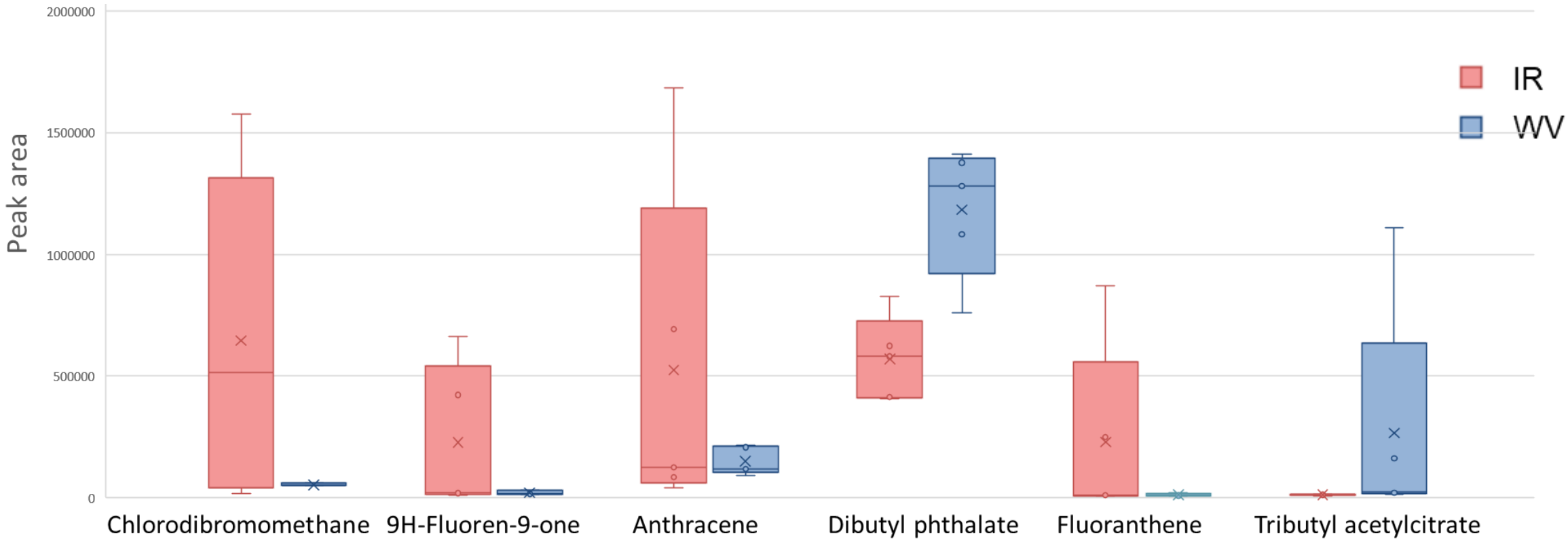
NIST20

Library Match score >75

** - known or probable carcinogens*

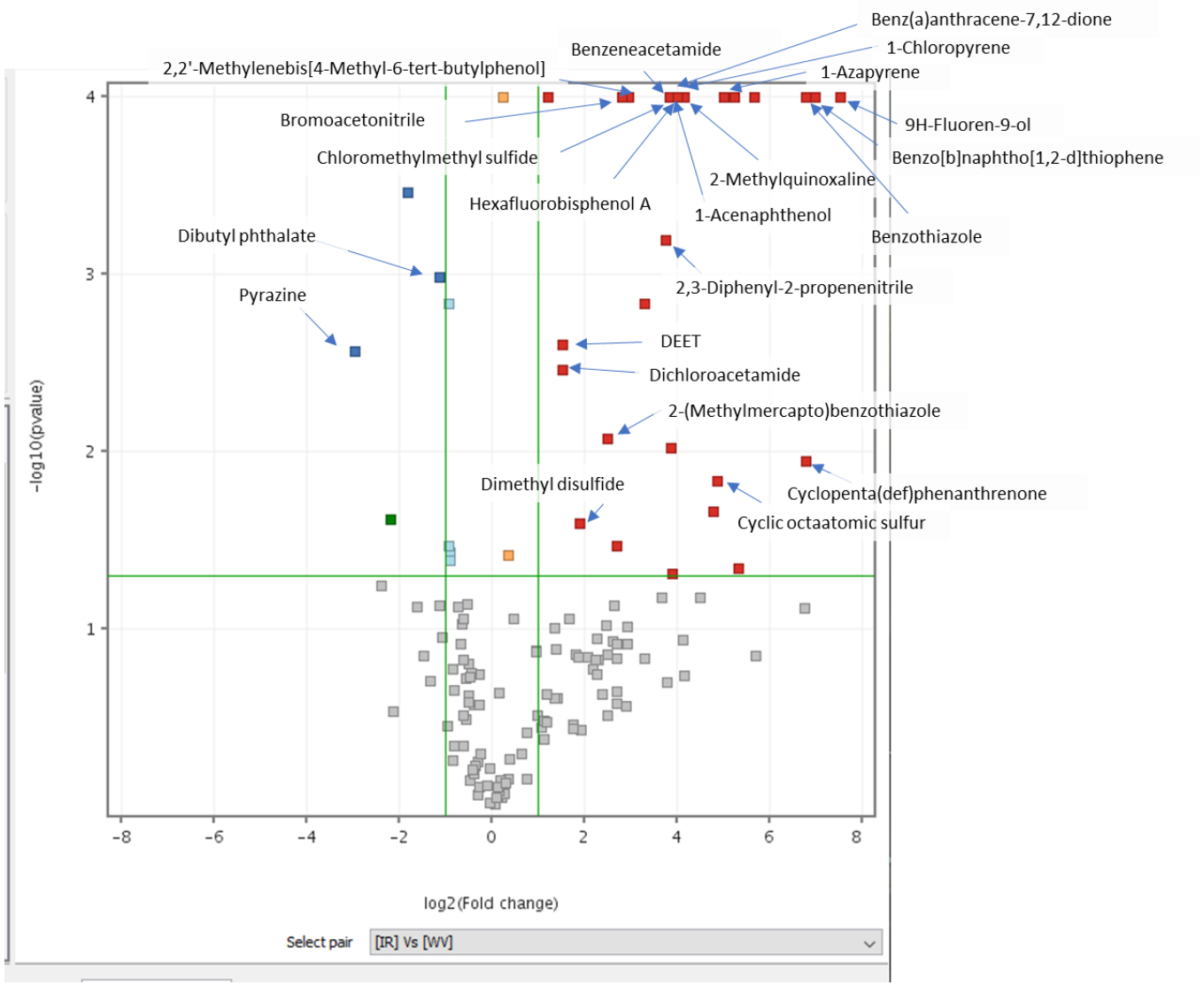
Pesticides and environmental contaminants PCDL

High Abundance Contaminants in Drinking Water Samples



IR: Irvine
WV: Weaverville
N = 5

Comparison of Water Sourced in Irvine vs Weaverville



Irvine vs Weaverville Water

Log of fold change (cut-off 2)
vs. log of p-Value (cut-off 0.05)

Conclusions

- PFAS accurate mass library containing over 100 EI spectra has been created for high resolution GC/Q-TOF including several emerging volatile PFAS
- PFAS compounds have been identified in soil and water extracts using PFAS PCDL
- Additional contaminants have been identified in drinking water from two different source categories and included disinfection byproducts, chemicals from personal care products, drugs, pesticides and other industrial contaminants without re-injecting the sample

Acknowledgements & Reference

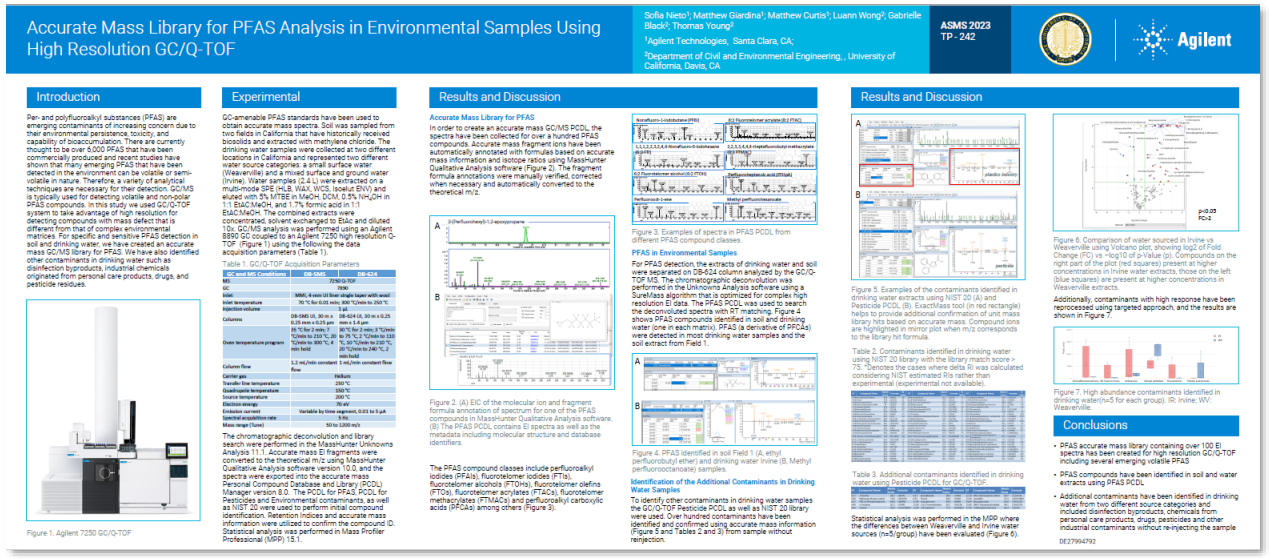
UC DAVIS
UNIVERSITY OF CALIFORNIA

Tom Young's team

Agilent

Matthew Curtis
Andrew McEachran

ASMS 2023 Poster: TP-242



Accurate Mass Library for PFAS Analysis in Environmental Samples Using High Resolution GC/Q-TOF

Sofia Nieto[1]; Matthew Giardina[1]; Matthew Curtis[1]; Luann Wong[2]; Gabrielle Black[2]; Thomas Young[2]

[1]Agilent Technologies, Santa Clara, CA;

[2]Department of Civil and Environmental Engineering, , University of California, Davis, CA

ASMS 2023 TP - 242

Introduction

Experimental

Results and Discussion

Results and Discussion

Conclusions

CONTACT:

Sofia Nieto: sofia.nieto@agilent.com

Tarun Anumol: tarun.anumol@agilent.com

Thank you!