

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

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Tarun Anumol¹, Sofia Nieto¹, Matthew Giardina¹,
Luann Wong², Gabrielle Black², Thomas Young²

¹ Agilent Technologies Inc.

² University of California - Davis



Background

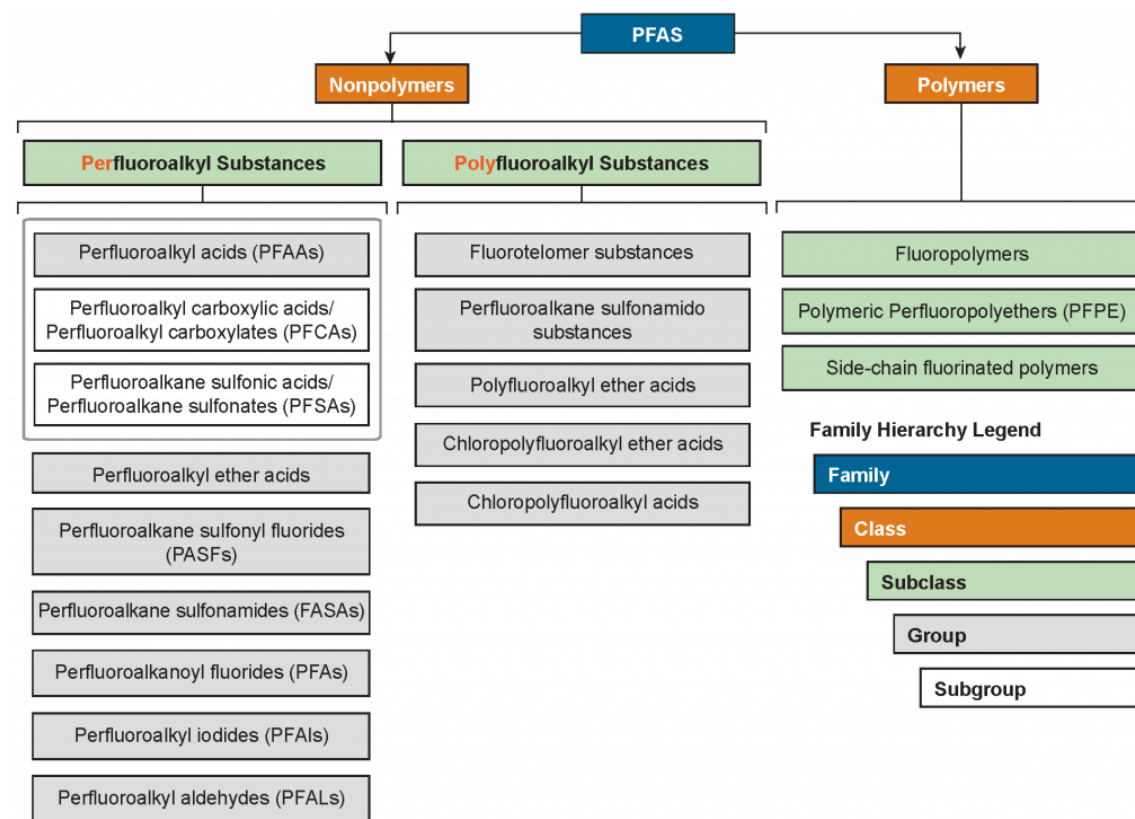
Per- and polyfluoroalkyl substances (PFAS) are emerging contaminants that are found in water, air, soil as well as wildlife

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

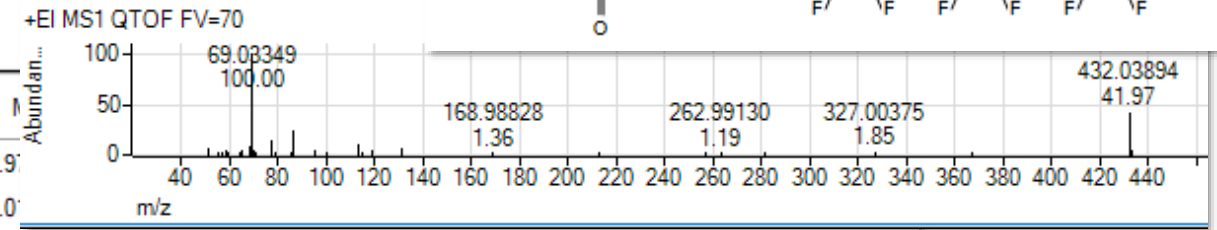
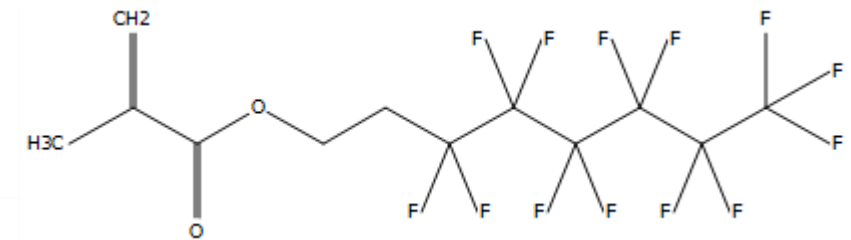


PFAS Family & Classes

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

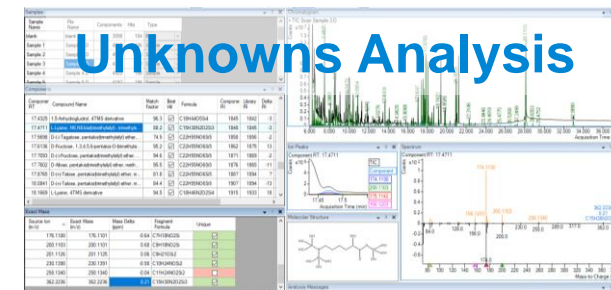
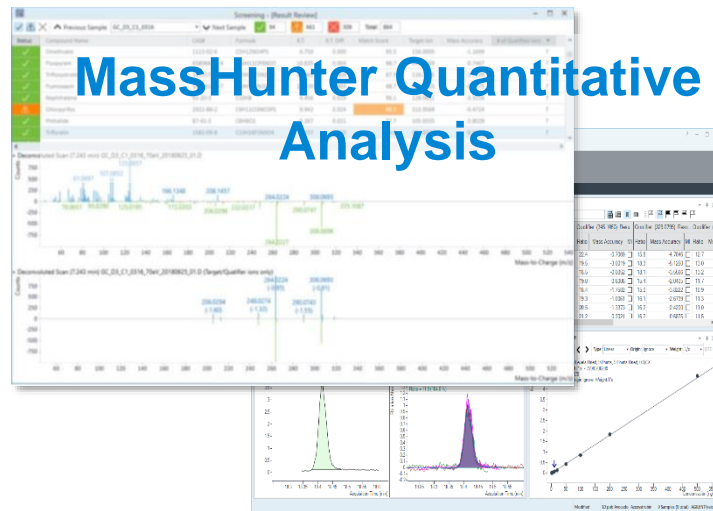
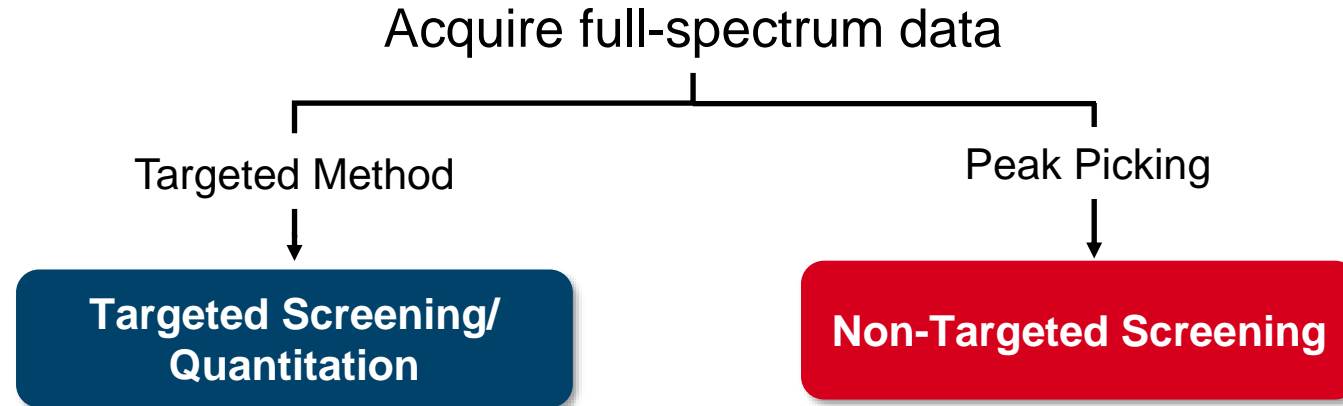
Accurate Mass GC/MS Libraries

- ❖ 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

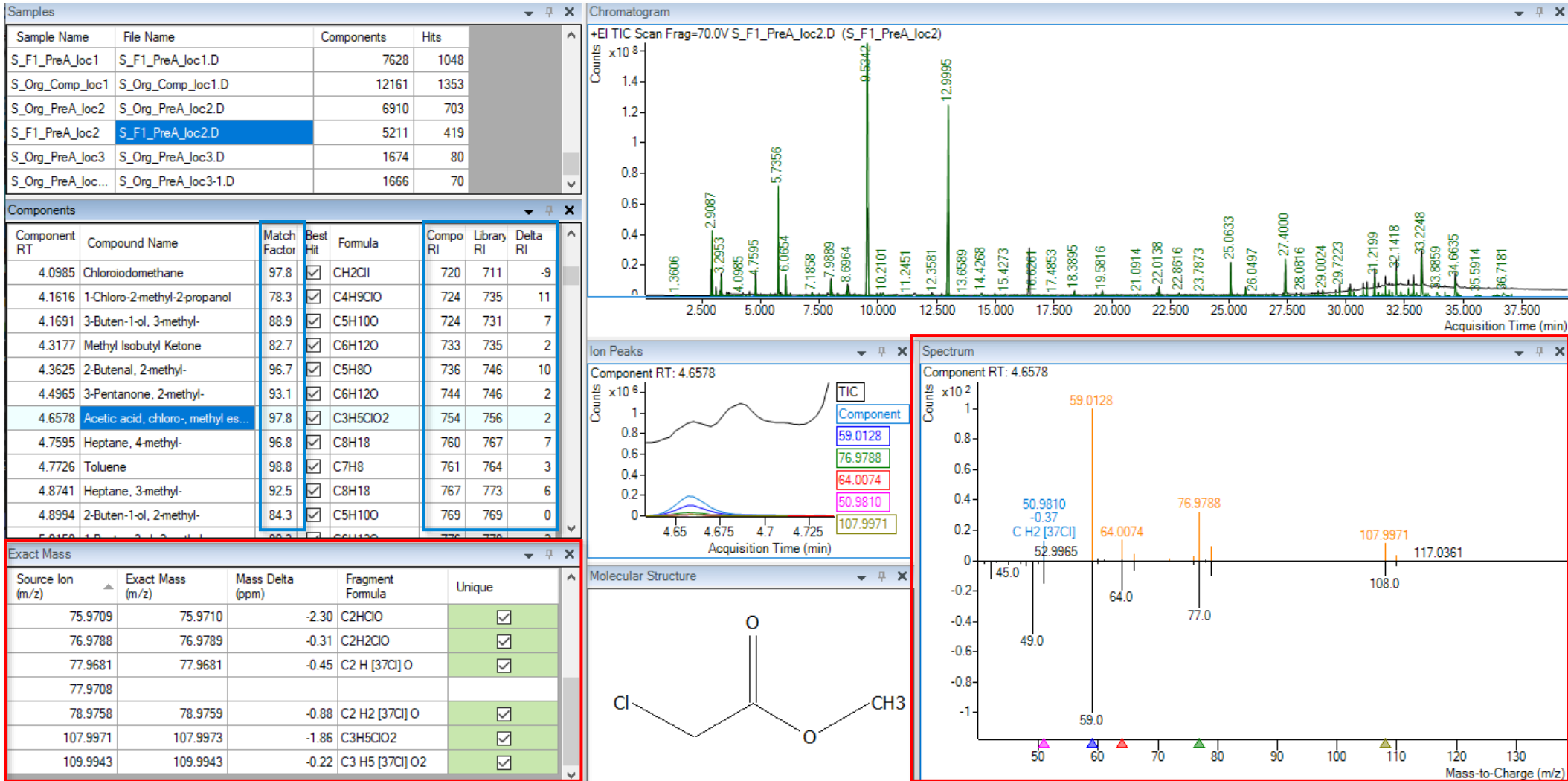


Name	Formula	Abundance	m/z	Library ID	Library Name
2,2-Difluoroethyl triflate	C3H3F5O3S	213.9			
Flurotyl	C4H4F6O	182.0			
4H-Perfluorobutanoic acid	C4H2F6O2	195.9959	14.354	679-12-9	DTXSID50892417
PFlUnDA / Perfluoroundecanoic acid (PFlUnA)	C11HF21O2	563.96412	6.124	2058-94-8	全氟十一烷酸; Perfluoro-n-undeca...
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



Non-Targeted Screening Workflow

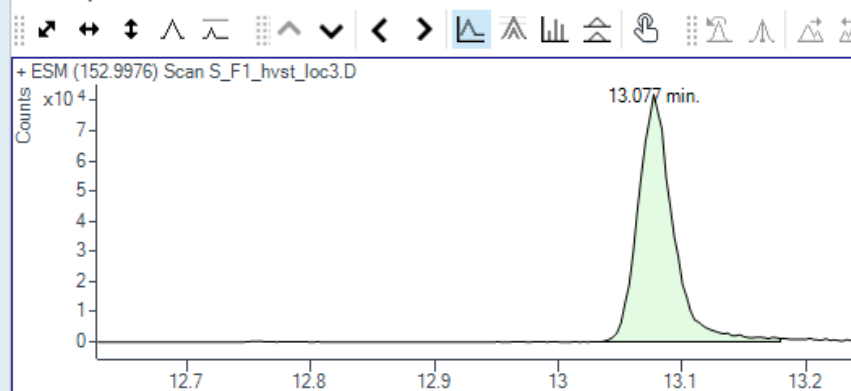


Target/Suspect Screening and Quantitation

Detailed Results table

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



Screening - [Result Review]

Targets: 88 Suspects: 88 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...
✓	<input type="checkbox"/>	Benzo[e]pyrene	192-97-2	C20H12	33.484	0.125		95.5	252.0934	0.6061	3
✓	<input type="checkbox"/>	Benzo[a]pyrene	50-32-8	C20H12	33.484	0.306		94.2	252.0934	0.6061	2
✓	<input type="checkbox"/>	Perylene	198-55-0	C20H12	33.484	0.649		95.4	252.0934	0.6061	3
✓	<input type="checkbox"/>	DNP / Dinonyl phthalate	84-76-4	C26H42O4	31.374	3.391		88.4	149.0233	2.0384	3
✓	<input type="checkbox"/>	Indeno[1,2,3-cd]pyrene	193-39-5	C22H12	36.443	1.461		90.2	276.0934	-0.6308	6
⚠	<input type="checkbox"/>	Imibenconazole	86598-92-7	C17H13Cl3N4S	28.986	9.028		24.5	125.0153	-1.9246	2
✓	<input type="checkbox"/>	Benzo[ghi]perylene	191-24-2	C22H12	36.443	2.285		90.8	276.0934	-0.6308	6

+ Deconvoluted Scan (36.450 min) S_F1_PreA_loc2.D

+ Deconvoluted Scan (36.450 min) S_F1_PreA_loc2.D (Target/Qualifier ions only)

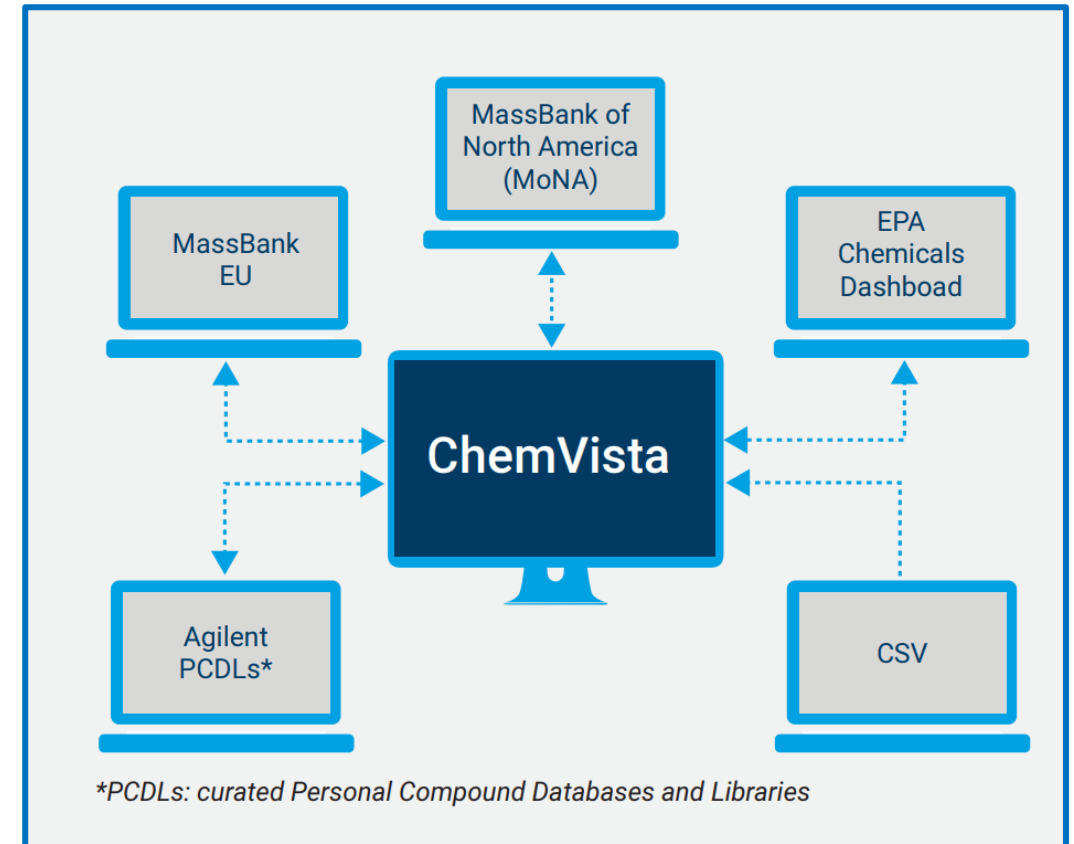
Deconvoluted spectrum

PCDL spectrum

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.

The screenshot displays the ChemVista Library Manager interface. The main window shows a search results table with columns for Formula, CAS, Mass, InChIKey, Agilent ID, Spectra Count, ChemSpider, and PubChem. The entry for Metolachlor-OXA is highlighted. To the right, the chemical structure of Metolachlor-OXA is shown, along with its CAS number (152019-73-3) and other identifiers. Below the structure, there are tags for classification, such as 'Pesticide degradate' and 'Environmental contaminant'. The bottom panel shows 'Export Options' and 'Spectral Filters' for refining the data.

Formula	CAS	Mass	InChIKey	Agilent ID	Spectra Count	ChemSpider	PubChem	
C24H17C2N2O4	79889-71-4	311.07487	STMHPFOOD	800	6	39833		
Oxetamin-carboxylate	C24H24NO4	18727-45-8	284.17361	NEPPTFHCK	9158	5	399259	448361
Isothioate	C7H17O3PS	36614-38-7	260.01283	SPONFOWE2	20568	0	34393	
Benodanone (Aladin)	C21H38N	30238-35-5	304.30043	CYDRTMLKJ	6896	3	8424	
Dymorphone	C17H19NO4	76-43-5	301.13141	UQDNDGZDF	2282	3	4447650	
Dimethachlor	C13H18NO2	55353-08-7	255.10261	SCDNDGKVDZ	592	8	36319	39722
Alachlor ESA	C14H21NO3S	14280-53-9	315.11404	UTCJGJGQYVA	9244	3	103108	
Fenamiphos	C13H22NO3PS	22224-92-6	303.3058	ZCPDREHLL	920	3	28827	
Trimethoprim	C14H18N4O3	738-70-5	290.13789	EDVHCERACR	1800	3	5376	
Lorsopram	C13H18C2N2O	846-48-1	320.01191	DJWJHQRVFI	403	5	3821	
N-Benzyloxy-Tamadol	C14H21NO2	91115-27-4	235.15723	QJFFHMBDL	5	231296	305678	
Isi-aceyl-sulfamethoxazole	C12H13NO4S	31132-10-7	295.06268	GKPIJZCALH	7844	5	58771	65280
Metolachlor-OXA	C15H21NO4	152019-73-3	278.14706	LNDDYCKMK	20043	8	2117088	1584202
Metazachlor-ESA	C14H17NO4S	17960-62-2	323.09388	IPVCEFEVHK	9372	5	2829024	8629102
2,7-Naphthalene disulfonic acid (Fosf)	C10H6O6S2	92-43-1	287.87623	VILFKYKHVY	9345	0	60073	
Perindole	C15H23NO2	55512-33-9	378.11688	JTCTMAVAHI	1359	6	37831	
17alpha-Estradiol (Alfatradol)	C18H24O2	57-95-0	272.17783	VOZDWFVQ	7571	3	61840	
Ofloxacin	C15H20FN3O3	113617-63-3	395.14568	QJFQDPLWV	7335	3	54631	
PCP / Phenoclidine	C17H25N	77-10-1	243.1987	JTMMGYZDZ	2791	3	6224	
Ruamitol	C17H12CPN2O	63284-71-9	314.06222	SAGTCDSDGF	2563	3	82786	
Promazine	C17H20N2S	58-40-2	284.15472	ZGUBHURJLS	3895	3	4257	
Ribavirin	C12H12NO5	36791-06-5	284.08077	HYLQVSLKAC	6316	8	36439	
Isoarbofos	C13H16NO4PS	24353-63-5	288.05377	YFVQKJBGZ	1850	3	82490	
Mevastatin	C23H34O5	33973-88-3	390.24062	ALJFQPRVWJ	4821	3	58182	
Dimethenamid-OXA	C12H17NO4S	38042-53-9	271.08783	HOYQASTVAC	9371	5	2829025	8629064
Propiconazole(I)	C15H17C2N2O	60207-90-1	341.06978	STJVVWVWQ	1746	9	39402	

Export Options

Export as: PCDL (*.cds)

Only compounds with spectra

Only most recent spectra for substance/method

Only compounds with unequivocally defined formula/mass

Exclude spectra

Exclude compound-level RTs

Spectral Filters

RIES ---paraton technique

Ionization technique: EM

Mass analyzer: POSITIVE

Collision energy: []

Source type: []

MS level: []

Method label: HPLC C18 Method 1 March 2023

Summary

Substances	1402
Substances with spectra	962
Substances with RTs	180
Substances with method data	1078
Spectra	3681

Start export

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.

Using ChemVista to Enhance Identification Workflows

Import GCMS spectra from MassBank of North America (MoNA)

Import Files

Select a source type and files to import

Source type: SDF (*.sdf)

Select file(s): Open file(s) 1 files selected

Create list on import:

List name: MoNA GCMS Spectra

Description: All GCMS spectra exported from MoNA (MassBank of North America)

Apply method label to imported data:

Import selected files

List: MoNA GCMS Spectra

Loaded 9750 of 9750 substances

Substance Name	Formula	CAS	Mass	InChIKey	Agilent ID	Spectra Count
PARA-TOLYLACETIC ACID METHYL ESTER	C10H12O2	164.08373	164.08373	LSAGWGNEL		1
PARA-TOLYLACETIC ACID TRIMETHYLSYL ES	C12H18O2S1	222.10761	222.10761	LXDPPIKXOU		1
PARA-TRIMETHYLSULFENAMETHYLDISILA	C14H28S13	280.14988	280.14988	WRLCOHGVN		1
Paraxanthine	C7H8N4O2	611.59-6	180.06473	QUNWUOVFR		1
PARA-XYLENE	C8H10	106-42-3	106.07825	URL8WVHYL		3
PARA-TOLUENESULFONAMIDE	C7H9NO2S	173.1054	173.1054	LQWIKVZFP		2
P-RENDOUQUINONE DIOXIME	C9H10N2O2	105.11-3	118.04289	LKHURILYF		1
PCB 101	C12H5Cl5	3760-79-2	323.88339	LAHWLEDBAD		1
PCB 138	C12H4Cl6	35065-29-2	357.84442	RFUJZMGNLZ		1
PCB 180	C12H3Cl7	35065-29-3	391.80544	WBHQLPUM		4
PCB 209	C12Cl10	2051-24-3	493.68853	QNRZLFDMA		1
PCB 28	C12H7Cl3	7012-37-5	255.96133	BZTNGSGZH		7
PCB 52	C12H6Cl4	35693-99-3	289.92236	HCWZFKLVW		2
p-Chlorobenziline	C8H8ClN	127.01888	127.01888	QSNCSYFYD		4
P-CHLOROBENZALDEHYDE	C7H5ClO	140.00289	140.00289	AVPQCSLYSF		1
P-CHLOROTOLUENE	C7H7Cl	106-43-4	126.02363	NFDACUSDTO		5
p-Coumaric acid	C9H8O3	501.98-4	164.04734	NSQWKAQJW		3
P-CRESOL	C7H8O	106-44-5	108.05751	IWDCLIOBJJ		5
p-Cresol sulfate	C7H8O4S	188.01433	188.01433	WONAKZGLSJ		1
P-CRESYL BUTYRATE	C11H14O2	178.09938	178.09938	RKRBABFDR		1
P-CRESYL ETHYL ETHER	C9H12O	136.08882	136.08882	WSPWHNNH		2
P-CRESYL FORMATE	C8H10O2	136.05243	136.05243	NEANJUMQAX		1
P-CRESYL HEPTANOATE	C14H20O2	220.14483	220.14483	AGUWVFPVY		1
P-CRESYL ISOBUTYRATE	C11H14O2	178.09938	178.09938	UPPISGDKAW		1
P-CRESYL ISOVALERATE	C12H16O2	192.11503	192.11503	MYDPTWHTU		1
P-CRESYL OCTANOATE	C19H22O2	294.36398	294.36398	ALYHNTLYYRI		1
P-CRESYL VALERATE	C12H16O2	192.11503	192.11503	XDFPFPKFPY		1
P-CINNONENZALDEHYDE DIMETHYLACETAL	C10H13NO2	177.07898	177.07898	KARLOZLJNG		1
P-CYMBE-N-OL	C10H14O	150.10447	150.10447	XLPDYISDR		1
P-DIETHOXYBENZENE	C10H14O2	166.09938	166.09938	VWGNVQBY		2
RELIGONALDEHYDE	C9H10O	134.19-6	142.13577	GVHFUZHODE		6
PENDIMETHALIN	C13H19N3O4	281.13756	281.13756	CHFOBRWCN		2
PENCILIN S-OXIDE	C28H28N2O5S	502.15624	502.15624	MFRHCHLMD		1
PENTACHLORONITROBENZENE	C6Cl5NO2					
Pentachlorophenol	C6Cl5O					
PENTACHLOROPHENYL ACETATE	C8Cl5O2					
PENTACHLOROPHENYL-TRIMETHYLSILANE	C9HCl5Si					

Current user: MICHAEL ANDREW (Agilent USA), Active project: Default

PCB 101

ClC1=CC(=CC(=C1)C(Cl)=CC2=CC(Cl)=CC(Cl)=C2)

CAS: 3760-79-2
Formula: C12H5Cl5
InChI: InChI=1S/C12H5Cl5/(13-6-3-2-9)(14)(15-6)(8-4-11)(16)(17)(18)(15-10)(15-11)S1
InChIKey: LAHWLEDBADHUGA-UHFFFAOYSA-N
Mass: 323.88339
SMILES: ClC1=CC(=CC(=C1)C(Cl)=CC2=CC(Cl)=CC(Cl)=C2)C1
Synonyms: 1,2,4-trichloro-5-(2,5-dichlorophenyl)benzene; 2,2',4,5,5'-Pentachlorobiphenyl

Number of spectra: 1

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

Export to PCDL for MassHunter Data Analysis Workflows

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	

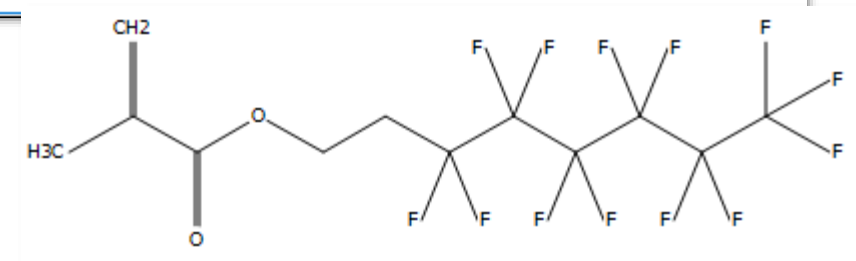
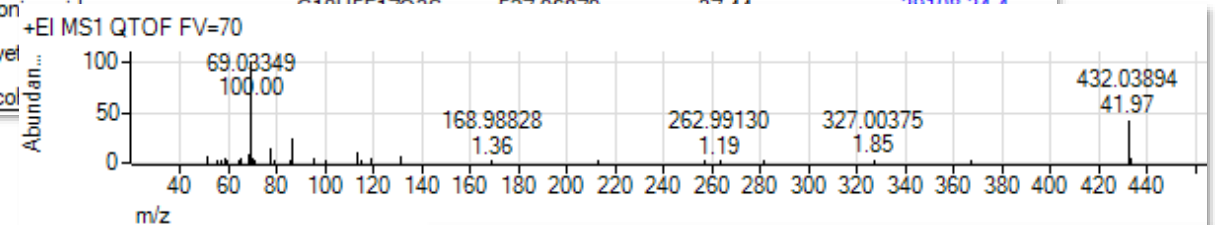


7250 GC/Q-TOF

Accurate Mass PFAS Library for GC/Q-TOF

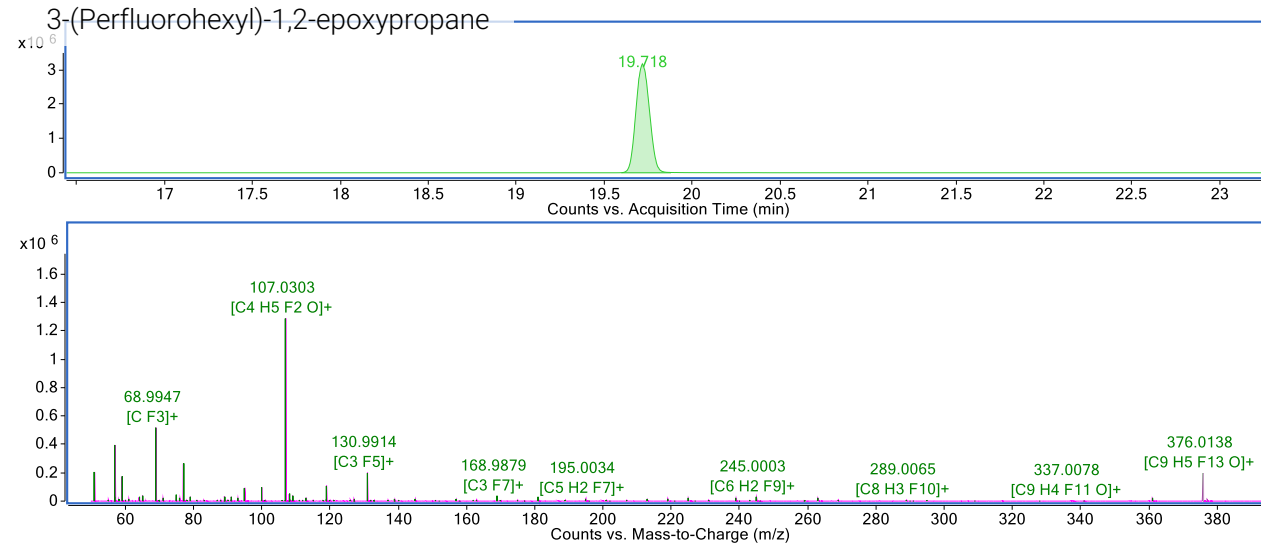
- ❖ Contains high resolution accurate mass spectra of over a hundred PFAS compounds (~140)
- ❖ Expert curated and converted to theoretical m/z
- ❖ Retention Time
- ❖ Molecular structures
- ❖ CAS and other identifiers

Name	Formula	Mass	Retention Time	CAS
2,2-Difluoroethyl triflate	C3H3F5O3S	213.97231	12.25	74427-22-8
Fluorotyl	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 sulfonate	C18H11F19O3S	567.00878	37.11	30100-34-4
N-Methyl-N-(2-hydroxyethyl)perfluorooctanamide	C12H11F8NO2	351.05412	36.783	30100-34-4
11:1 Fluorotelomer alcohol	C17H13F17O	469.0395	36.783	30100-34-4

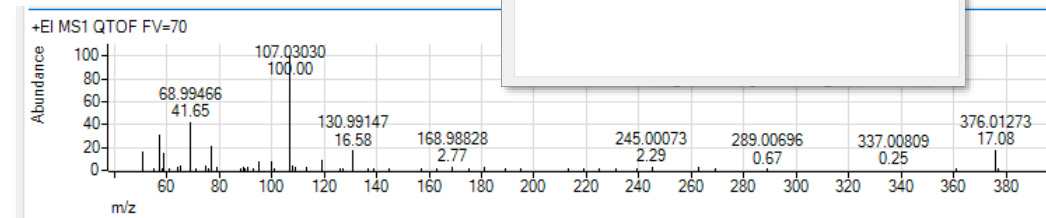
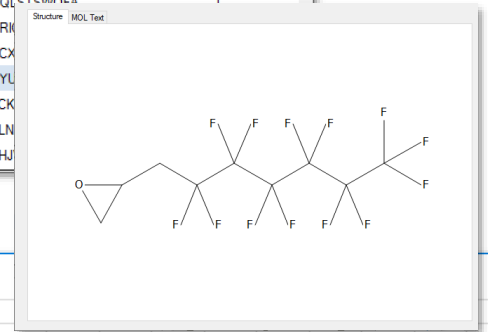


Creation of the Accurate Mass PCDL

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

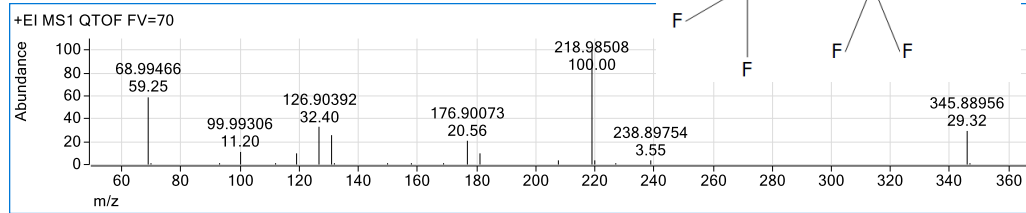
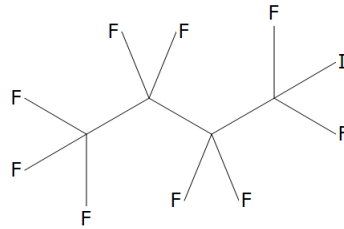


Name	Formula	Mass	Retention Time	CAS	IUPAC	SMILES	InChI Key	InChI	NumSpectra
Perfluoro-3,6,9-trioxatridecanoic acid	C10HF19O5	561.95206	18.85	330562-41-9	Difluoro{1,1,2,2,...	OC(=O)C(F)(F)OC(...	GDQLCTCWOEA		1
1-(Perfluorooctyl)propane-2,3-diol 2	C11H7F17O2	494.01746	18.89	94159-84-9	4,4,5,5,6,6,7,7,8...	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)(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...	KGYL...		
3-(Perfluoropropyl)propanol	C6H7F7O	228.03851	20.206	679-02-7	4,4,5,5,6,6,6-Hep...	OCCCC(F)(F)C(F)C...	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)C(F)...	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...	KEHU...		

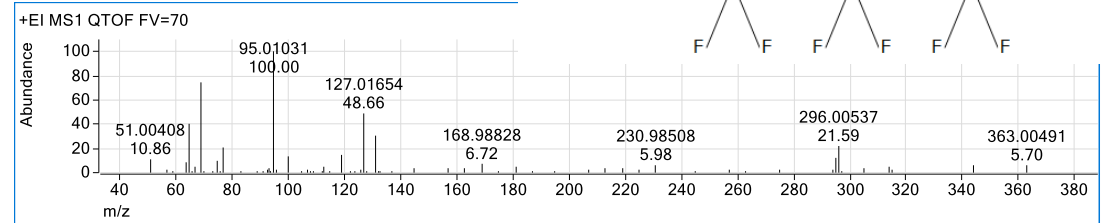
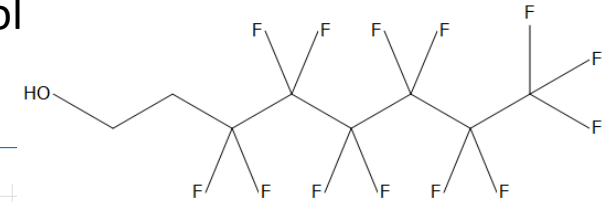


PFAS Classes in the PCDL

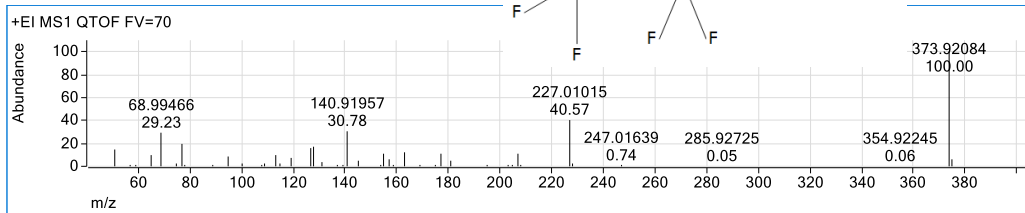
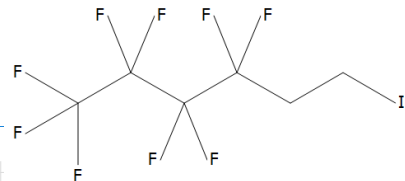
Nonafluoro-1-iodobutane (PFBI)



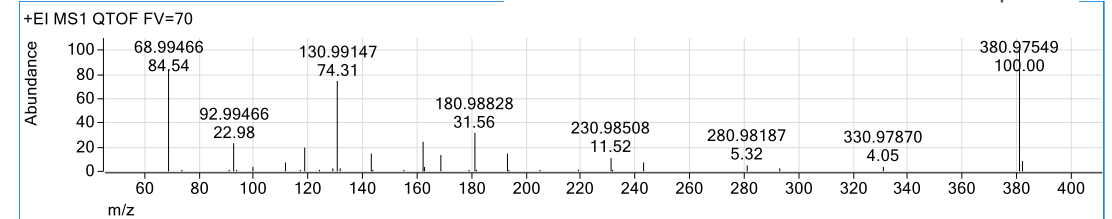
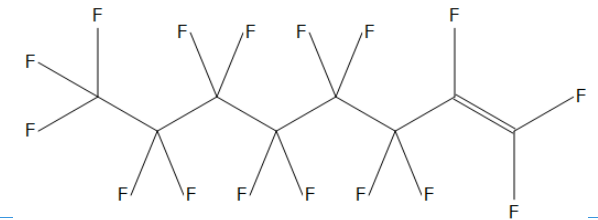
6:2 Fluorotelomer alcohol (6:2 FTOH)



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

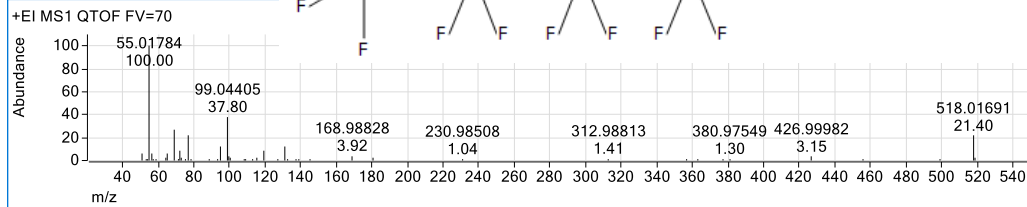
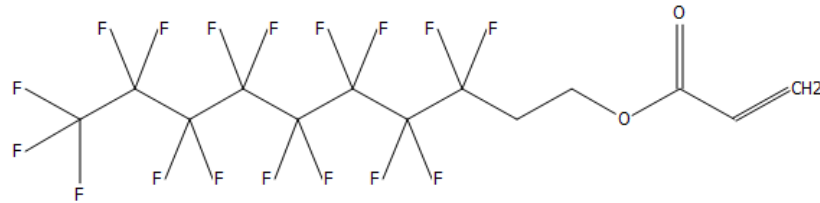


Perfluorooct-1-ene

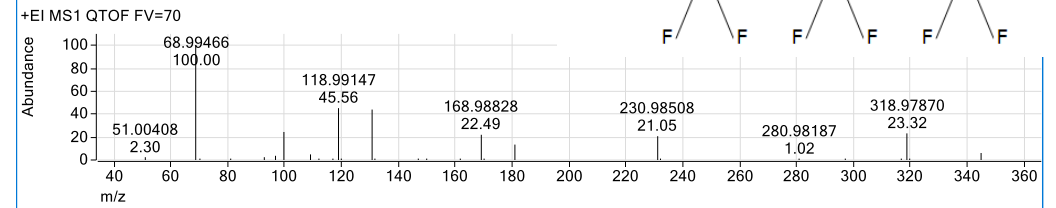
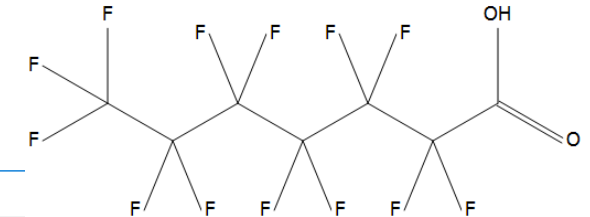


PFAS Classes in the PCDL

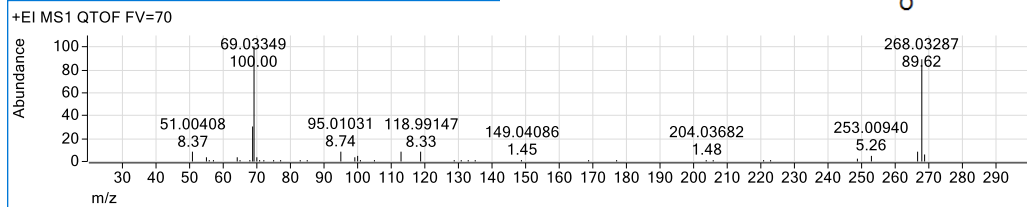
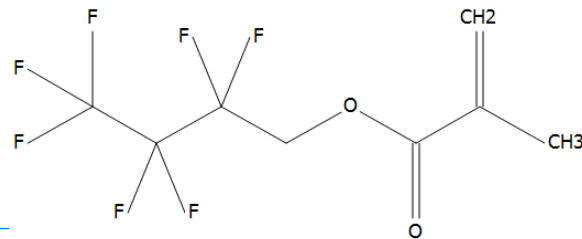
8:2 Fluorotelomer acrylate (8:2 FTAC)



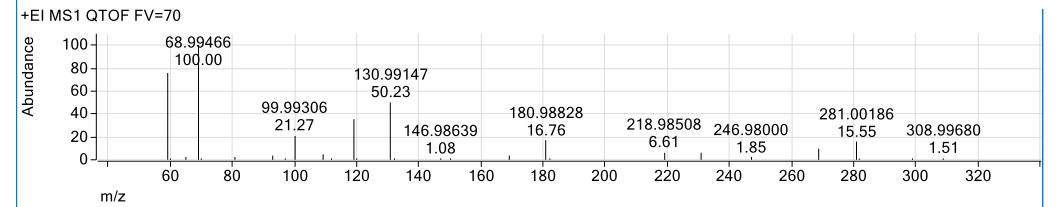
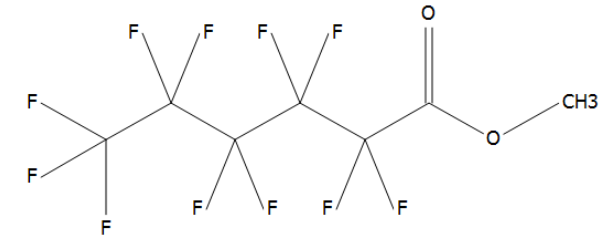
Perfluoroheptanoic acid (PFHpA)



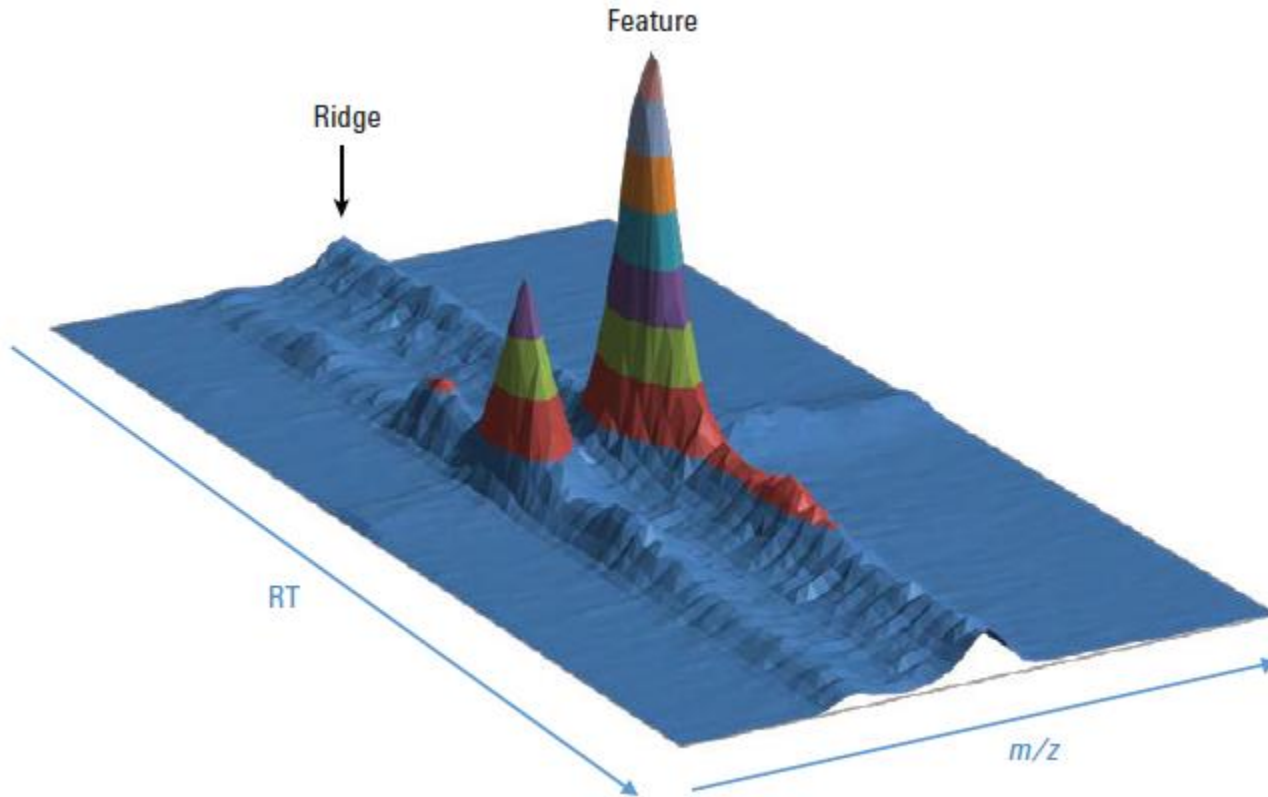
2,2,3,3,4,4,4-Heptafluorobutyl methacrylate (3:1 FTMAC)



Methyl perfluorohexanoate



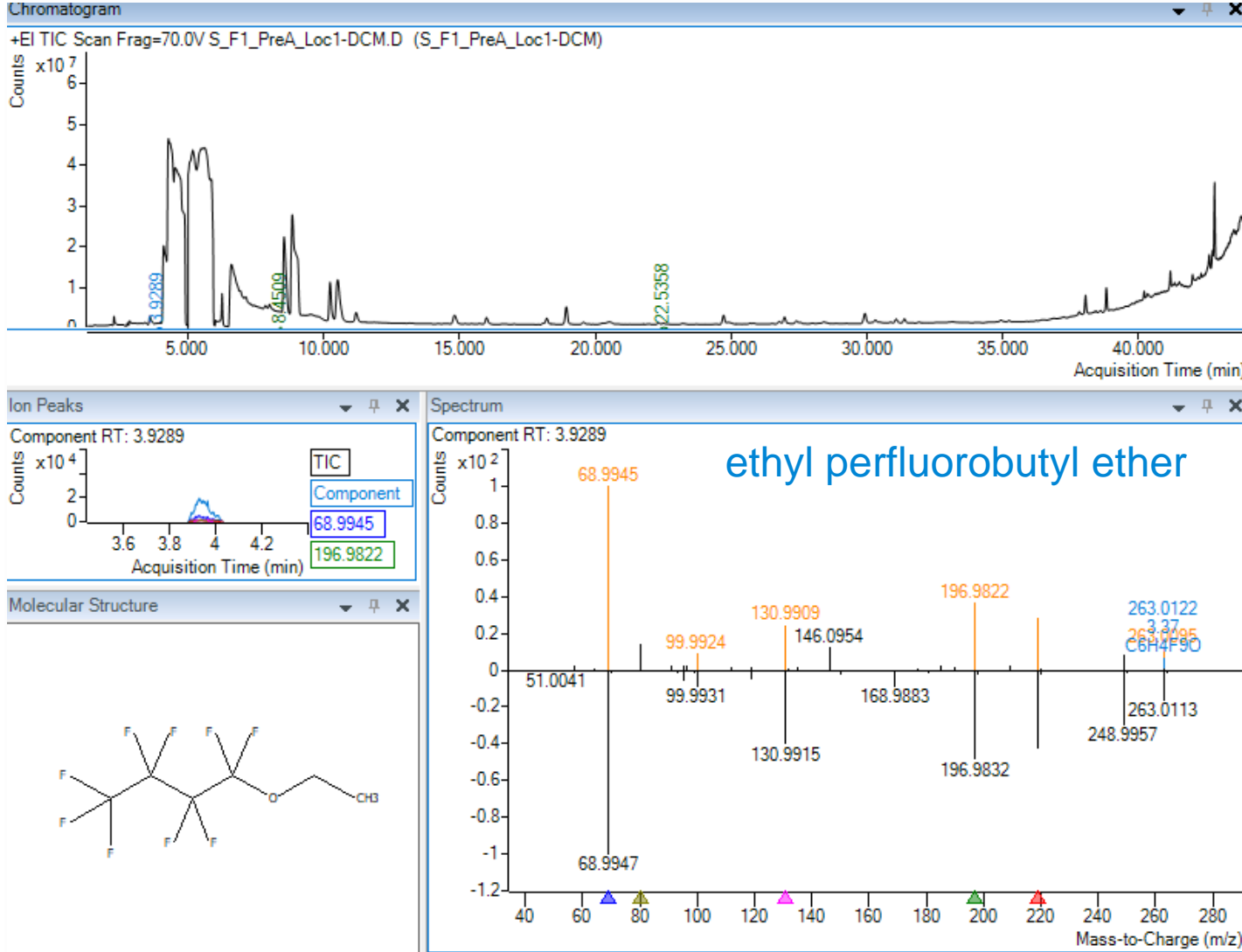
SureMass Deconvolution and Library Search



SureMass signal processing

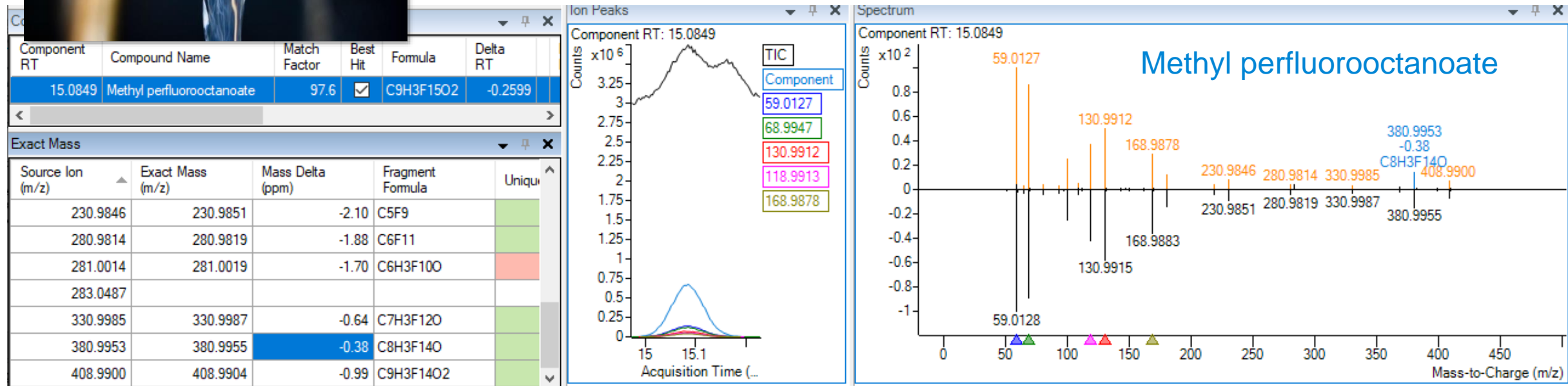
Examples of PFAS Identified in Soil and Water Using the PFAS PCDL

Sample: soil extracted from Field 1



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

Sample: drinking water (Irvine)



Additional Contaminants in Drinking Water Samples

Sample Name	File Name	Compon	Hits	Type
IR01-S	IR01-S.D	4541	1012	Sample
IR02-W	IR02-W.D	4590	1045	Sample
IR05-W	IR05-W.D	4532	1063	Sample
IR10-S	IR10-S.D	4277	1018	Sample

Compone RT	Compound Name	Match Factor	Best Hit	Formula
31.3270	Pyridine-3-carbonitrile, 1,2-dihydro-5-acet...	68.7	<input checked="" type="checkbox"/>	C13H10N2OS2
31.3776	Phthalic acid, di(2-propylpentyl) ester	94.8	<input checked="" type="checkbox"/>	C24H38O4
31.4007	2,3,4',6-Tetrabromodiphenyl ether	72.6	<input checked="" type="checkbox"/>	C12H6Br4O
31.4122	2-[5-(3,4,5-Trimethoxyphenyl)-1H-1,2,4-tri...	68.8	<input checked="" type="checkbox"/>	C13H14N4O3
31.4796	Bis[3,4-dichlorophenyl]sulfone	81.1	<input checked="" type="checkbox"/>	C12H6Cl4O2S

Source Ion (m/z)	Exact Mass (m/z)	Mass Delta (ppm)	Fragment Formula	Uniqu
200.1062				
353.8825	353.8837	-3.46	C12H6Cl4O2S	<input checked="" type="checkbox"/>
355.8806	355.8808	-0.39	C12 H6 Cl3 [37Cl]...	<input checked="" type="checkbox"/>
356.8838				
357.8769	357.8778	-2.52	C12 H6 Cl2 [37Cl]...	<input checked="" type="checkbox"/>

Pesticides PCDL

NIST20

Component RT	Compound Name	Match Factor	Best Hit	Formula
20.4110	Pentachlorobenzene	71.2	<input checked="" type="checkbox"/>	C6HCl5
20.5636	Dibenzofuran	89.1	<input checked="" type="checkbox"/>	C12H8O
21.4543	DEET / Diethyltoluamide	61.8	<input checked="" type="checkbox"/>	C12H17NO
21.6887	DEP / Diethyl phthalate	97.1	<input checked="" type="checkbox"/>	C12H14O4
21.8494	2-Undecanone	59.3	<input checked="" type="checkbox"/>	C11H22O
22.2919	DPA / Diphenylamine (DFA)	84.7	<input checked="" type="checkbox"/>	C12H11N
22.4348	Isoxadifen	90.8	<input checked="" type="checkbox"/>	C16H13NO3
22.6068	TBP / Tributylphosphate	76.9	<input checked="" type="checkbox"/>	C12H27O4P
23.5151	HCB / Hexachlorobenzene	95.8	<input checked="" type="checkbox"/>	C6Cl6
23.8069	Flurenol-butyl	59.9	<input checked="" type="checkbox"/>	C18H18O3
24.4644	Dibenzothiophene	88.8	<input checked="" type="checkbox"/>	C12H8S
24.6400	Benzylbenzoate	73.5	<input checked="" type="checkbox"/>	C14H12O2
24.8971	Anthracene	94.0	<input checked="" type="checkbox"/>	C14H10
24.9175	TCPD / Tri-(2-chloroisopropyl)phosphate	83.6	<input checked="" type="checkbox"/>	C9H18Cl3O4P

Source Ion (m/z)	Exact Mass (m/z)	Mass Delta (ppm)	Fragment Formula	Unique
76.0306	76.0308	-1.77	C6H4	<input checked="" type="checkbox"/>
77.0386	77.0386	-0.08	C6H5	<input checked="" type="checkbox"/>
78.0418				
91.0542	91.0542	-0.61	C7H7	<input checked="" type="checkbox"/>
105.0335	105.0335	-0.23	C7H5O	<input checked="" type="checkbox"/>
105.0697	105.0699	-1.75	C8H9	<input checked="" type="checkbox"/>

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

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

NIST20

Library Match score >75

* - *known or probable carcinogens*

Pesticides and environmental
contaminants PCDL

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

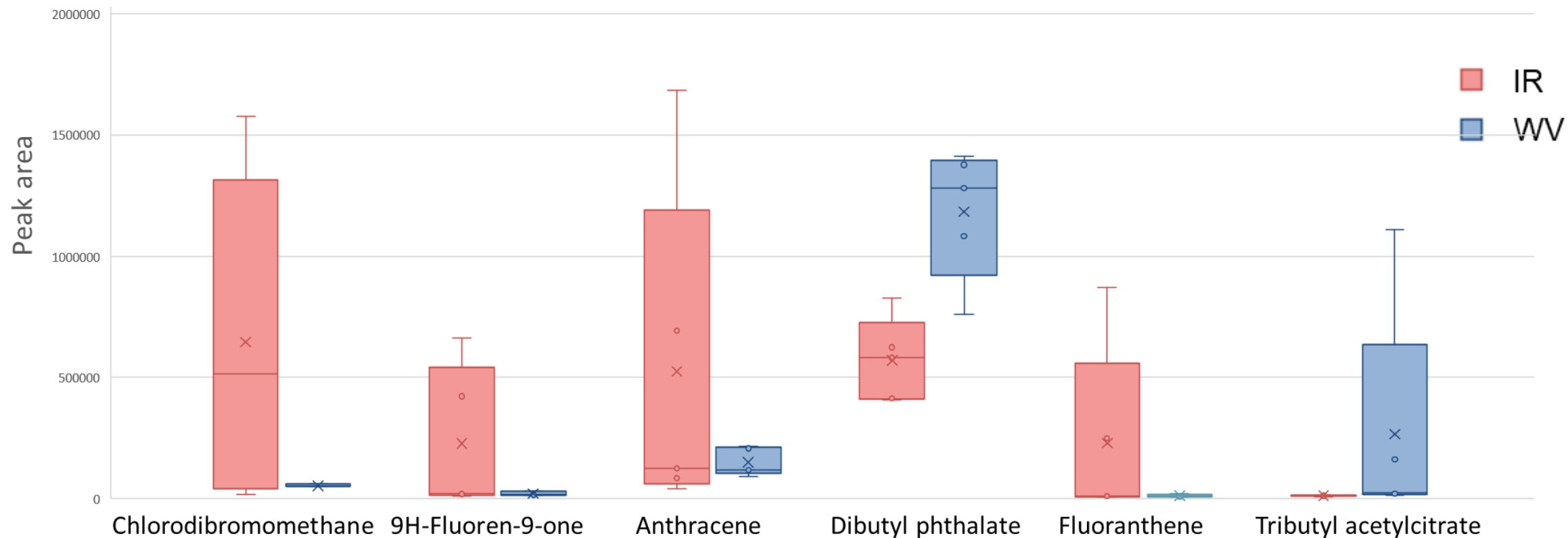
NIST20

Library Match score >75

* - *known or probable carcinogens*

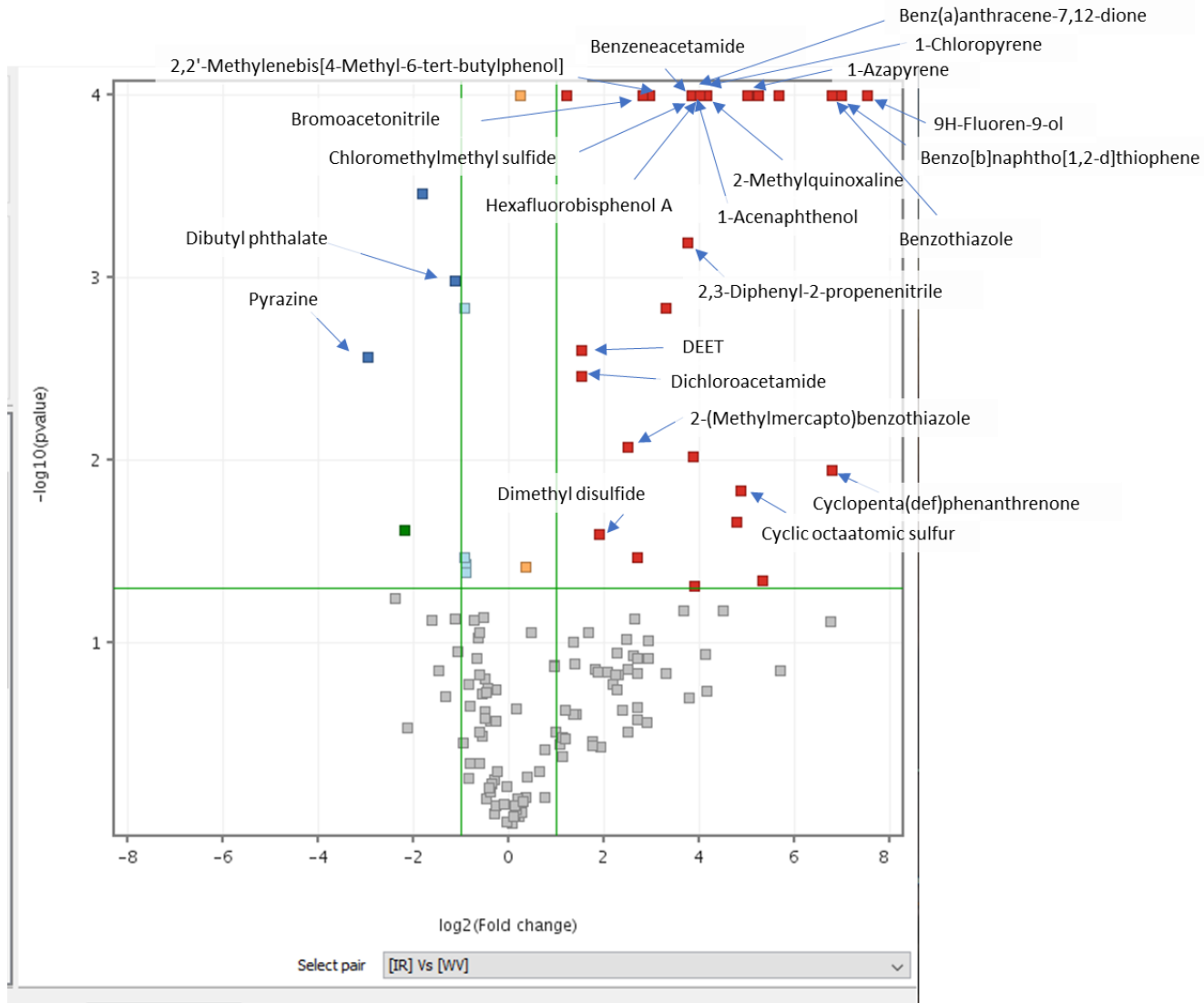
Pesticides and environmental
contaminants PCDL

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



Tom Young's team

Matthew Curtis
Andrew McEachran



ASMS 2023 Poster: TP-242

CONTACT:

Sofia Nieto: sofia.nieto@agilent.com

Tarun Anumol: tarun.anumol@agilent.com

Sofia Nieto¹, Matthew Gardina¹, Matthew Curtis¹, Luenn Wong¹, Gabriella Blasko¹, Thomas Young¹
¹Agilent Technologies, Santa Clara, CA
²Department of Civil and Environmental Engineering, University of California, Davis, CA
ASMS 2023 TP-242

Introduction

Per- and polyfluoroalkyl substances (PFAS) are emerging contaminants of increasing concern due to their environmental persistence, toxicity, and capability of bioaccumulation. There are currently thought to be over 5,000 PFAS that have been commercially produced and recent studies have shown that many emerging PFAS that have been detected in the environment can be volatile or semi-volatile in nature. Therefore, a variety of analytical techniques are necessary for their detection. GC/MS is typically used for detecting volatile and non-volatile PFAS compounds. In this study we used GC/QTOF system to take advantage of high resolution for detecting compounds with mass defect that is characteristic of perfluorinated compounds. For specific and sensitive PFAS detection in soil and drinking water, we have created an accurate mass GC/MS library for PFAS. We have also identified other contaminants in drinking water such as disinfection byproducts, industrial chemicals, and pesticide residues.

Experimental

GC-amenable PFAS standards have been used to obtain accurate mass spectra. Soil was sampled from two fields in California that have historically received biosolids and extracted with methylene chloride. The drinking water samples were collected at two different locations in California and represent two different water source categories: a small surface water (Weaverville) and a mixed surface and ground water (Inyue). Water samples (2.4 L) were extracted on a multi-mode SPE (H.E. WAX, WCL, Isolute ENV) and eluted with 0.1 M HCl, 100% MeOH, 0.5 M NaCl in 100% MeOH, and 1.7% formic acid in 1:1 EtAc:MeOH. The combined extracts were concentrated, solvent exchanged to EtAc and diluted 10x. GC/MS analysis was performed using an Agilent 8890 GC coupled to an Agilent 1260 high-resolution QTOF (Figure 1) using the following data acquisition parameters (Table 1).

Table 1. GC/QTOF Acquisition Parameters	
GC and MS Conditions	GC 8890
GC	1260
MS	1260
Sample	Meth. 6.00 min; 0.50 min; 2.00 min; 1.00 min
Inlet Temperature	300 °C for 0.50 min; 250 °C for 0.50 min
Injection Volume	1.00 µL
Carrier Gas	99.999% He, 0.01% H ₂ , 0.001% N ₂
Column	DB-5MS, 30 m x 0.25 mm x 0.25 µm
Flow Rate	1.00 mL/min
Temperature Program	Initial 100 °C, 5 min; 100 °C to 200 °C, 1 min; 200 °C to 250 °C, 1 min; 250 °C to 300 °C, 1 min; 300 °C to 320 °C, 1 min; 320 °C to 350 °C, 1 min; 350 °C to 400 °C, 1 min; 400 °C to 450 °C, 1 min; 450 °C to 500 °C, 1 min; 500 °C to 550 °C, 1 min; 550 °C to 600 °C, 1 min; 600 °C to 650 °C, 1 min; 650 °C to 700 °C, 1 min; 700 °C to 750 °C, 1 min; 750 °C to 800 °C, 1 min; 800 °C to 850 °C, 1 min; 850 °C to 900 °C, 1 min; 900 °C to 950 °C, 1 min; 950 °C to 1000 °C, 1 min
Column Flow	1.00 mL/min
Carrier Gas	99.999% He, 0.01% H ₂ , 0.001% N ₂
Transfer Line Temperature	250 °C
Injection Temperature	250 °C
Source Temperature	250 °C
Detector Temperature	250 °C
Sample Concentration	Variable from 0.01 to 1.00 µg/L
MS Resolution	100,000
MS Scan Rate	10,000 scans/sec

The chromatographic deconvolution and library search were performed in the MassHunter Unknowns Analysis 11.1. Accurate mass E⁺ fragments were converted to the theoretical m/z using MassHunter Qualitative Analysis software version 10.0, and the spectra were exported into the accurate mass spectra were exported into the accurate mass spectra in MassHunter Qualitative Analysis software version 10.0. The PCOL for PFAS, PCOL for Pesticides and Environmental Contaminants, as well as 10,101 MS were used to perform initial compound identification. Retention indices and accurate mass information were utilized to confirm the compound ID. Statistical analysis was performed in Mass Profiler Professional (MPP) 15.1.

Results and Discussion

Accurate Mass Library for PFAS
In order to create an accurate mass GC/MS PCOL, the spectra have been collected for over a hundred PFAS compounds. Accurate mass fragment ions have been automatically annotated with formulae based on accurate mass information and isotopic ratios using MassHunter Qualitative Analysis software (Figure 2). The fragment formula annotations were manually verified, corrected when necessary and automatically converted to the theoretical m/z.

PFAS Environmental Samples
For PFAS detection, the extracts of drinking water and soil were separated on DB-5MS column analyzed by the GC/QTOF MS. The chromatographic deconvolution was performed in the Unknowns Analysis software using a SureSelect algorithm that is optimized for complex high resolution E+ data. The PFAS PCOL was used to search the deconvoluted spectra with MS matching (Figure 4) shows PFAS compounds identified in soil and drinking water (one in each matrix). PFAS (a derivative of PFOA) were detected in most drinking water samples and the soil extract from Field 1.

Identification of the Additional Contaminants in Drinking Water Samples
To identify other contaminants in drinking water samples the GC/QTOF Peptide PCOL, as well as NIST 20 library were used. Over hundred contaminants have been identified and confirmed using accurate mass information (Figure 5 and Table 2) from sample without rejection.

Results and Discussion

Conclusions

- PFAS accurate mass library containing over 100 E⁺ spectra has been created for high resolution GC/QTOF including several emerging volatile PFAS
- PFAS compounds have been identified in soil and water extracts using PFAS PCOL
- 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 rejecting the sample sources (n=1/group) have been evaluated (Figure 6).



Thank you!