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Analysis of PFAS and Other Environmental Contaminants in Soil and Oat Plants Using High Resolution GC/MS

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Introduction

Per- and polyfluoroalkyl substances (PFAS) are persistent synthetic organic pollutants with a potential to bioaccumulate. Soil is a significant reservoir of PFAS as well as of many other persistent environmental contaminants, and thus can contribute to contamination of ground water, atmosphere, and biota. Therefore, to better understand the source and transport of these contaminants, both soil and plant extracts have been evaluated. This study describes different approaches for extraction and analysis of PFAS and other environmental contaminants in soil and plants using the GC/Q-TOF.

To maximize the sensitivity of PFAS detection, the target screening approach based on PFAS accurate mass library was used. The PFAS PCDL used in this study included over 150 electron ionization (EI) PFAS spectra along with retention times (RTs) and retention indices (RIs).

In addition to PFAS, many persistent pollutants were identified in both soil and plants, where both target and nontarget screening workflows were used. These pollutants included pesticides, polyaromatic hydrocarbons (PAHs), PCBs, PBDEs, and flame retardants.

Figure 1. Agilent 7250 GC/Q-TOF

Experimental

Soil and oat plants were sampled from two fields in California (F1 and F2) that have historically received biosolids. The soil samples were collected prior to the application of biosolids (labeled PreA for preapplication). A certified USDA organic (Org) field was also sampled prior to treating the subplots with compost (Comp) and compost and lime (C&L). The compost was collected as well. The soil was also sampled at harvest time (Hvst).The soil and plant samples were either extracted with methylene chloride (DCM) for liquid injections or subjected to headspace solid-phase microextraction (HS-SPME, Table 1). GC/MS analysis was performed using an 8890 GC coupled to a 7250 high resolution Q-TOF (Figure 1) using the following the data acquisition parameters (Table 2).

Table 1. HS-SPME Conditions

Parameter	Value
Autosampler	Agilent PAL 3 CTC
Sample Volume	2 g + 2 mL water (soil); 1 g + 3 mL water (plant)
SPME Fiber	80 µm DVB/CWR/PDMS
Fiber conditioning	300 ˚C for 5 minutes
Sample Equilibration Time	10 minutes
Extraction Conditions	50 ˚C for 35 minutes
Agitator speed	300 rpm (10 seconds on, 2 seconds off)
Desorption Conditions	250 °C for 7 minutes

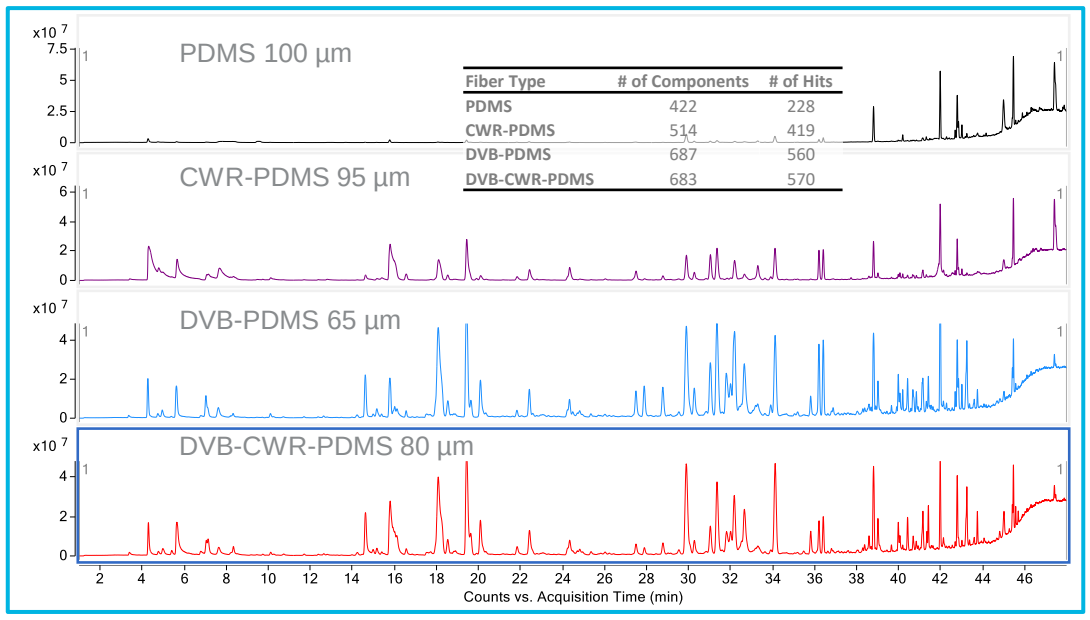
Table 2. GC/Q-TOF Acquisition Parameters

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)	*m/z* 50 to 1200	

The chromatographic deconvolution and library search were performed using MassHunter Unknowns Analysis software and the NIST23 EI library. The suspect screening was performed using the GC/Q-TOF Screener tool of MassHunter Quantitative analysis software and accurate mass libraries for Pesticides and PFAS.

Selection of SPME Fiber for Soil Analysis

Four different SPME fibers were evaluated for the ability to extract volatile compounds from soil. The test was performed using soil (2 g) sampled from the same location, mixed with 2 mL of water, and run under the same SPME conditions. TIC generated by each fiber tested are shown in Figure 2. Both DVB/PDMS and DVB/CWR/PDMS fibers produced a significant number of peaks and showed the ability to extract a wide range of compounds. The number of the identifiable peaks was slightly higher for DVB/CWR/PDMS.



Fiber Type	# of Components	# of Hits
PDMS	422	228
CWR-PDMS	514	419
DVB-PDMS	687	560
DVB-CWR-PDMS	683	570

Figure 2. SPME fiber performance on soil samples.

Detection of Volatile PFAS Using Accurate Mass PFAS Library

A few PFAS compounds were detected when analyzing the data from SPME. An example of a compound identified in a few soil and plant samples using the GC/Q-TOF Screener is shown in Figure 3. This compound is a volatile 6:2 fluorotelomer alcohol, frequently detected in environmental matrices.

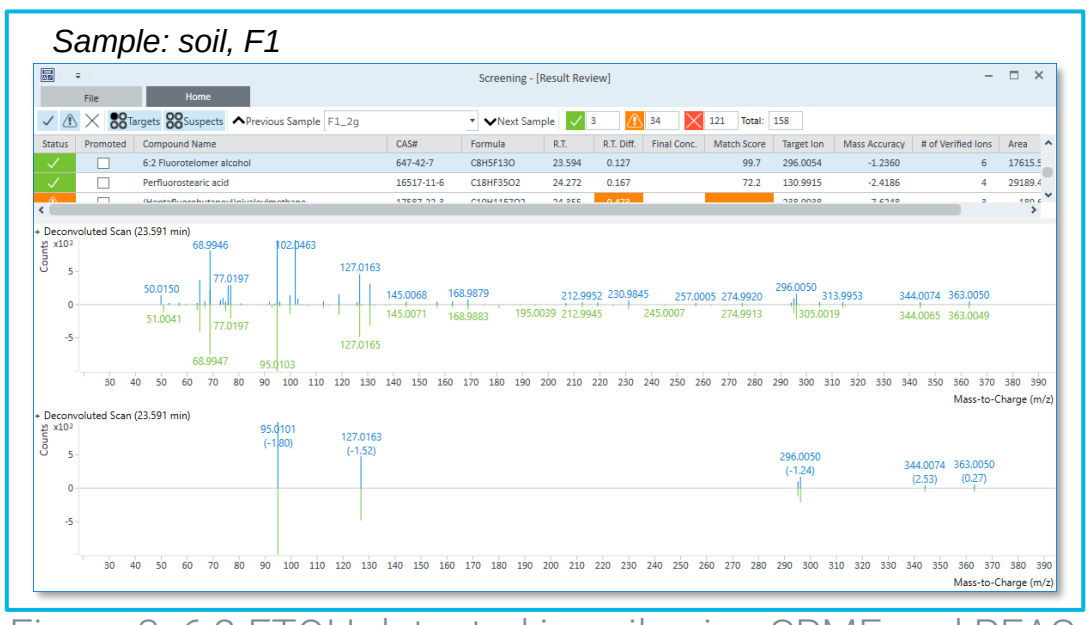


Figure 3. 6:2 FTOH detected in soil using SPME and PFAS PCDL-based screening approach. The mirror plot at the top shows deconvoluted compound spectrum versus the spectrum from the PFAS PCDL. The mirror plot at bottom displays only target and qualifier ions with mass accuracy in the parentheses.

When performing nontarget analysis, the SureMass deconvolution algorithm was used. It is optimized for high-resolution data to ensure high speed, sensitivity, and spectral integrity. While the suspect screening approach was able to detect more PFAS compounds, the abundant PFAS was detected in both approaches (Figures 4A and B). All the PFAS were identified in soil and plants using the PFAS PCDL.

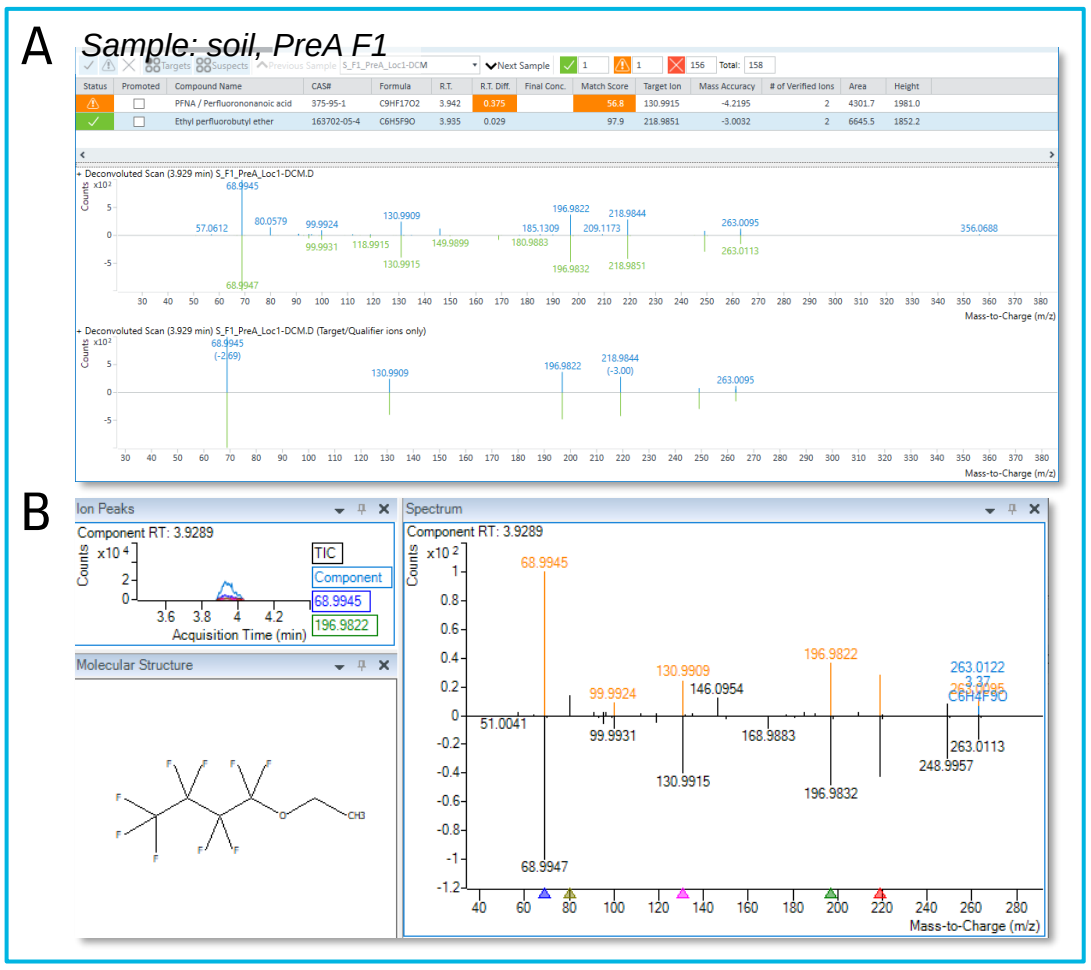


Figure 4. PFAS (ethyl perfluorobutyl ether) identified in DCM soil extracts using PFAS PCDL in both suspect screening (A) and a deconvolution-based approach (B).

The HS-SPME approach for PFAS extraction provided a higher number of identified volatile PFAS compounds. The amounts of PFAS detected (Table 3) were estimated based on the standard injections.

Table 3. PFAS detected in soil and plants by HS-SPME using the accurate mass PFAS PCDL and suspect screening approach. The estimated amounts (in pg on-column) are shown.

Compound	RT	Quant ion	Soil samples							Plant samples				
			F1 PreA	F1 Hvst	F2 Hvst	C&L Hvst	Compost Hvst	Org Hvst	Org Compost	F1	F2	Compost	C&L	Org
Ethyl perfluorobutyl ether	4.4	218.9851	150.2	-	-	-	-	-	-	-	-	-	-	-
6:1 Fluorotelomer alcohol	20.94	130.9915	-	2	-	-	-	-	-	2.2	-	-	-	-
6:2 Fluorotelomer alcohol	23.59	296.0054	-	7.5	0.3	-	-	-	6.9	2.5	-	-	-	-
N-Methylperfluorooctanesulfonamide	43.1	93.9957	0.3	3.4	0.9	2.1	0.4	1.2	0.9	0.2	-	-	-	-

Identification of Other Contaminants in Soil and Oat Plants

The separation was carried out using the DB-5ms UI column to be able to use the RI values from the extensive NIST23 library. After a quick prescreening, the identified pollutants were grouped by classes and approached separately.

Results and Discussion

PCBs and PBDEs were identified in the nontargeted approach (Figure 5). To eliminate false positives based on the accurate mass, the ExactMass tool was used (Figure 5A). PCBs and PBDEs were mostly detected in the soil extracts (Figure 5B). However, BDE-47 was detected in oat plant extract from F2.

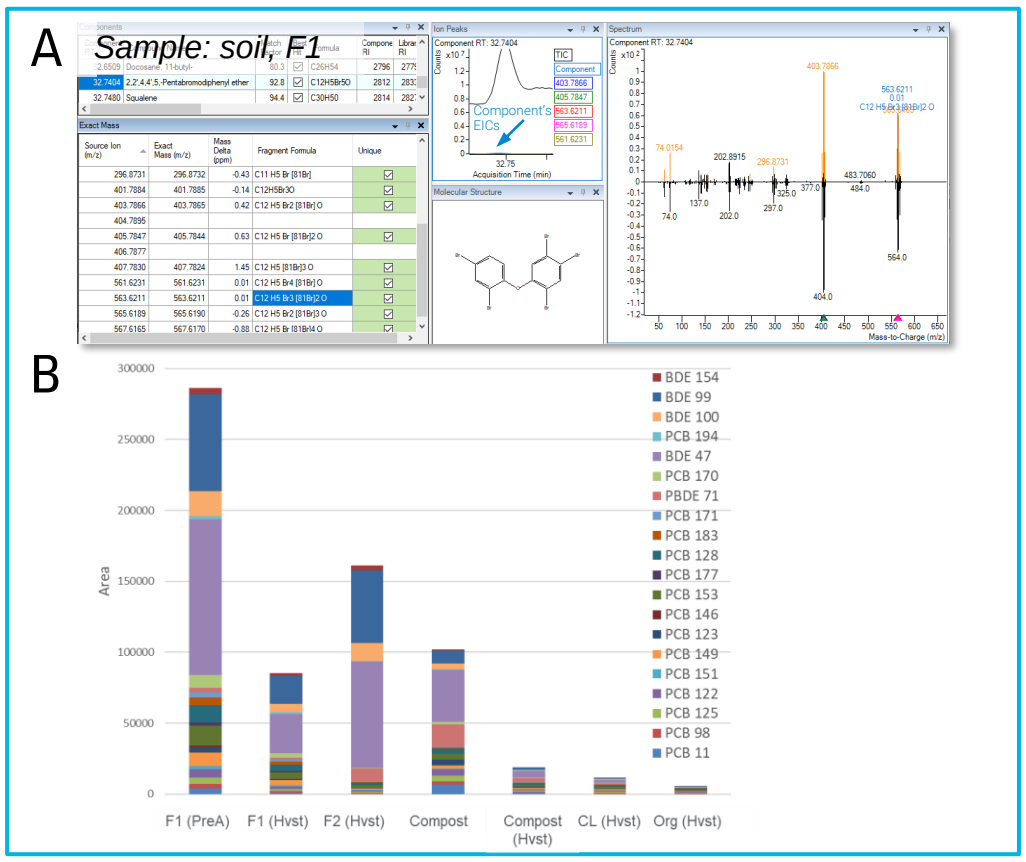


Figure 5. PCBs and PBDEs in soil DCM extracts. (A) An example of BDE detected in soil from Field 1 at the time of harvesting. ExactMass table (bottom left panel) shows how well the accurate mass fragment ions are matching the unit mass library hit providing the additional confirmation of compound ID. The most representative ions are highlighted in mirror plot when m/z matches the library hit formula. (B) Bar graph showing responses of PCB and PBDE for all the soil samples they have been identified.

50 pesticides were detected in soil extracts using the suspect screening with Pesticide PCDL (Table 4).

Table 4. Pesticides detected in soil by suspect screening and the accurate mass Pesticide PCDL.

Compound name	RT	RT delta*	Match Score**	F1 PreA	F1 Hvst	F2 Hvst	C&L Hvst	Comp Hvst	Org Hvst	Org Comp
Diuron Metabolite	16.56	0.28	99.9	x	x	x	x	x		x
1,2,3,5-tetrachlorobenzene	16.98	0.32	90.7	x						
2,4,6-Trichlorophenol	17.44	0.25	99.3				x	x	x	tr***
Nicotine	17.56	0.05	97.9							x
Lufenuron	18.71	0.22	99.7			x				x
3,4-Dichloroaniline	18.88	0.21	99.9	x	x	x				
Pentachlorobenzene	20.42	0.35	99.4	x	x					x
DEET / Diethyltoluamide	21.46	0.22	82.1	tr	tr	tr	x	x	tr	x
2,3,4,5-Tetrachloroanisole	22.74	0.32	99.8	x						x
Bromoxynil	23.14	0.09	99.9	tr			x	x		
HCB / Hexachlorobenzene	23.52	0.36	99.7	x	x	x	tr	x	x	x
Dichloran (Dicloran)	23.84	0.16	97.8		x	x				x
Swep (MCC)	24.27	0.1	85.6	x	x	x				
PCP / Pentachlorophenol	24.27	0.24	99.7				tr	x		x
Pyrimethanil	25	0.1	82.5					tr		x
Chlordene	25.1	0.03	98.5							x
Pentachloroaniline	25.74	0.24	99.7	x	x		x	x		x
Dithiopyr	26.85	0.4	93.7	x	x	x	x	x		x
Anthraquinone	27.59	0.05	99.7	x	x	x	x	x	x	x
4,4'-Dichlorobenzophenone	27.86	0.02	80.3	x						x
Fipronil sulfide	28.13	0.43	99.7			x	tr	x		x
Cyprodinil	28.27	0.05	99.1				tr	x		x
Diuron	28.28	0.31	78.1				tr	x		tr
Fluopyram	28.49	0.18	93				x	x		x
Chlorbenside	28.99	0.21	92.2	x	x	x				
Chlordane-trans	28.82	0.03	99.7	x	x	x	x	x	x	x
Triclosan	28.85	0.03	99.3	x	x	x		x		x
Chlordane-cis	29.06	0.04	99.9	x	x	x	x	x	x	x
Nonachlor-trans	29.11	0.07	99.9	x	x	x	x	x	x	x
Flutolanil	29.23	0.11	85.2					x		x
Fludioxonil	29.27	0.18	99.6							x
Dieldrin	29.5	0.05	84.6	x	tr	tr				
p,p'-DDE	29.42	0.04	99.2	x	x	x	x	x	x	x
Oxadiazon	29.43	0.14	97.7				x	x		x
o,p'-DDD (Mitotane)	29.52	0.07	99.9	x	x	x	tr	x	x	
Fipronil sulfone	29.34	0.33	98.6	tr		x	tr	x		x
Myclobutanil	29.48	0.11	98.8					x		x
p,p'-DDD	30.03	0.02	99.5	x	x	x	x	x	x	tr
Nonachlor-cis	30.03	0.04	99.9	x	x	x	tr	tr		x
Carfentrazone-ethyl	30.32	0.13	98.8			x				
Bromoxynil octanoate	30.39	0.06	88.4	x			x	tr		
Propiconazole I	30.43	0.11	96.4				x	x	tr	x
Chloridazon (PAC)	30.44	0.06	91.5					x		
Propiconazole II	30.5	0.04	96				x	x	tr	x
Tebuconazole	30.7	0.03	92.7				x	x		x
Chlorbenside sulfone	30.7	0.39	89.6		tr	tr	x	x		x
Bifenthrin	31.08	0.09	98.6	tr	x	tr	x	x	x	x
cis-Permethrin	32.19	0	99.1	x	x	x	tr	x	x	x
trans-Permethrin	32.28	0.01	81			x			tr	tr
Difenconazole II	34.09	0.01	88.9					tr		x

*RT delta is recalculated from RI
**Highest Match Score across the samples
***tr = trace, indicates Match Factor is < 75

PAHs are included into the Pesticide PCDL and were screened together with pesticides in a single workflow. PAHs were mostly detected in soil extracts (Figure 6). However, phenanthrene and fluoranthene were also identified in most plant samples.

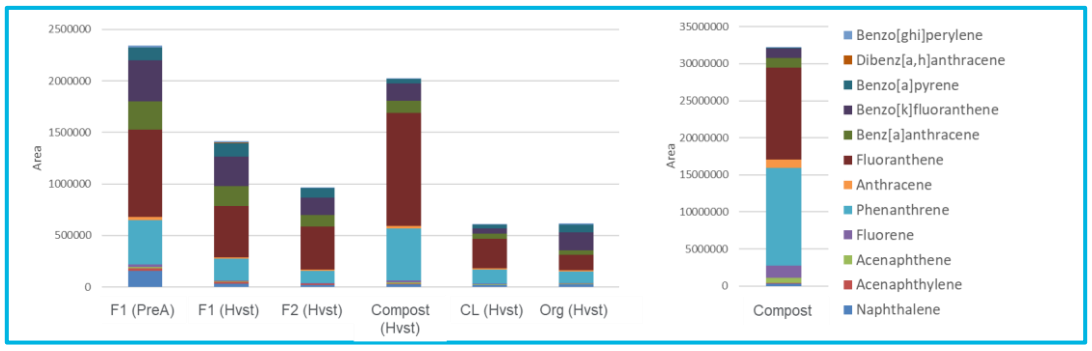


Figure 6. PAH detected in soil DCM extracts using the accurate mass Pesticide PCDL and suspect screening approach. Bar graph shows PAH peak area.

The accurate mass spectra for most flame retardants are included in the Pesticide PCDL. A couple of flame retardants identified in nontargeted analysis and missing in the Pesticide PCDL, were exported to the Quant method directly from the Unknowns Analysis and screened together with the rest of the targets (Figure 7).

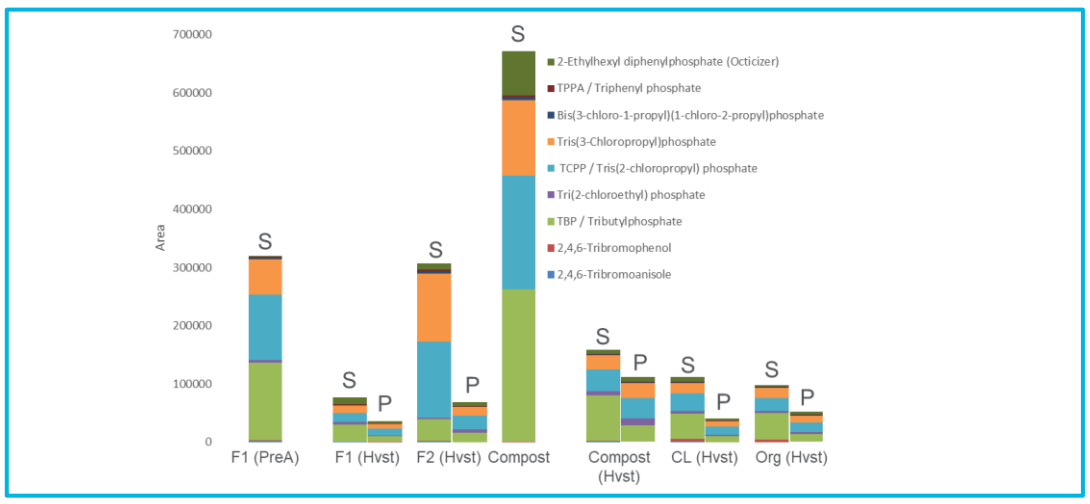


Figure 7. Flame retardants detected in soil and plant DCM extracts using a combined approach that included both accurate mass PCDL as well as NIST23 library. The bar graph shows flame retardants responses in soil (S) and plant (P) extracts.

Conclusions

- Various approaches for PFAS extraction from soil and plants as well as downstream data processing have been discussed. The most efficient and sensitive approach for volatile PFAS analysis in soil and plants was HS-SPME combined with the suspect screening based on the PFAS accurate mass PCDL and the GC/Q-TOF.
- Soil and plant extracts were also screened for other contaminants, and PCBs, PBDEs, PAHs, pesticides, and flame retardants were identified using targeted, nontargeted, and combined methodologies.

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