

Supplementary Materials for  
**Uncovering per- and polyfluoroalkyl substances (PFAS) with nontargeted ion  
mobility spectrometry–mass spectrometry analyses**

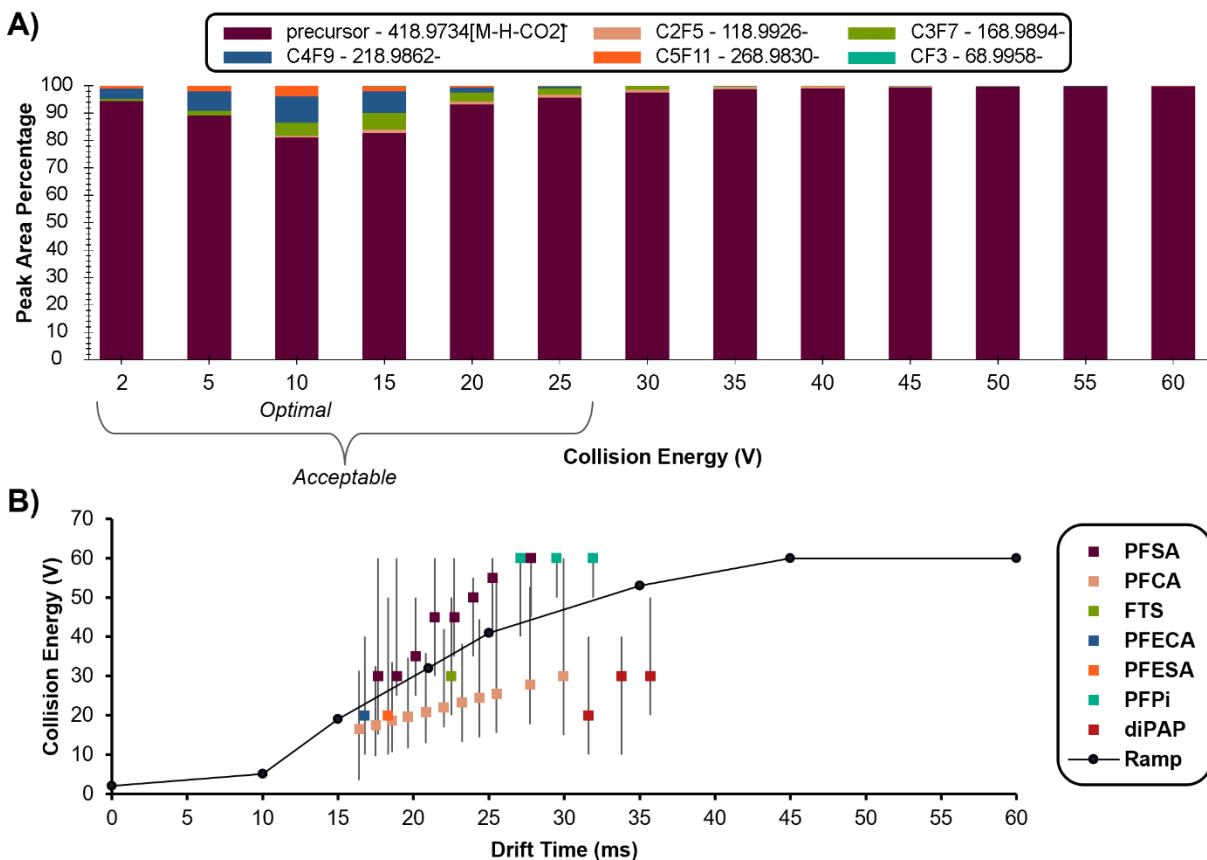
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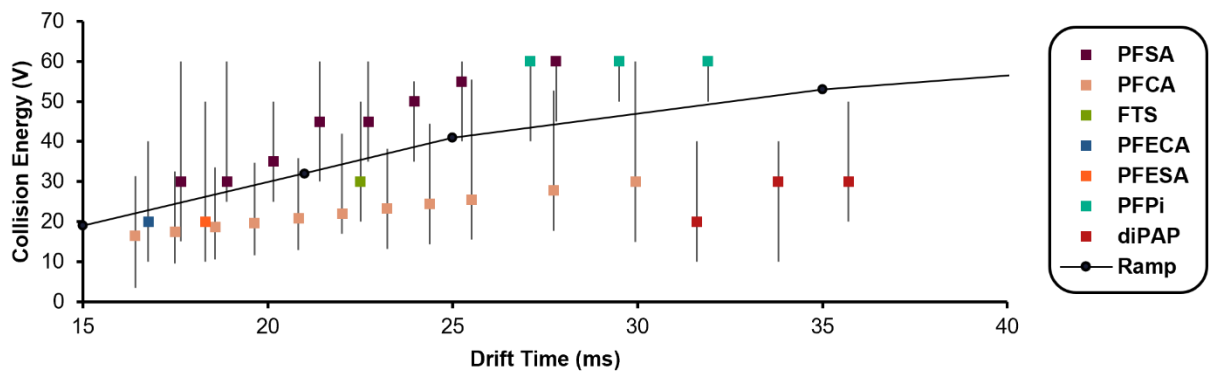
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Figs. S1 to S20  
Tables S1 to S5



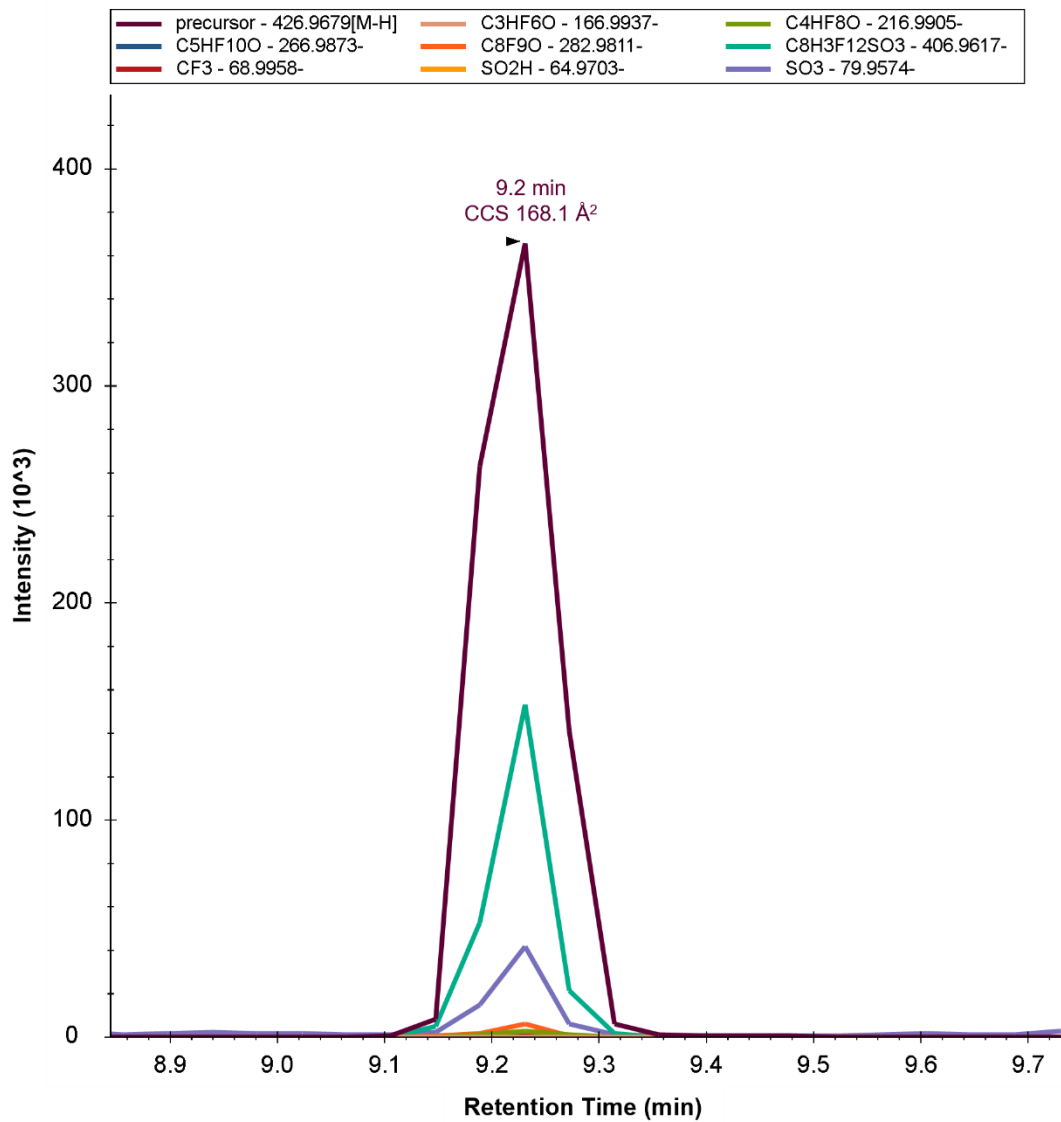
**Fig. S1.**

Collision energy (CE) ramp optimization. **(A)** Total peak area percentages of PFNA fragments demonstrating the determination of the optimal CE value (10 V) and acceptable CE range (2-25 V) for a given PFAS. **(B)** Drift time dependent CE ramp. The square point and “error bars” indicate the optimal CE value and acceptable CE range for each standard tested. The drift time plotted for each standard is the average value across all injections.



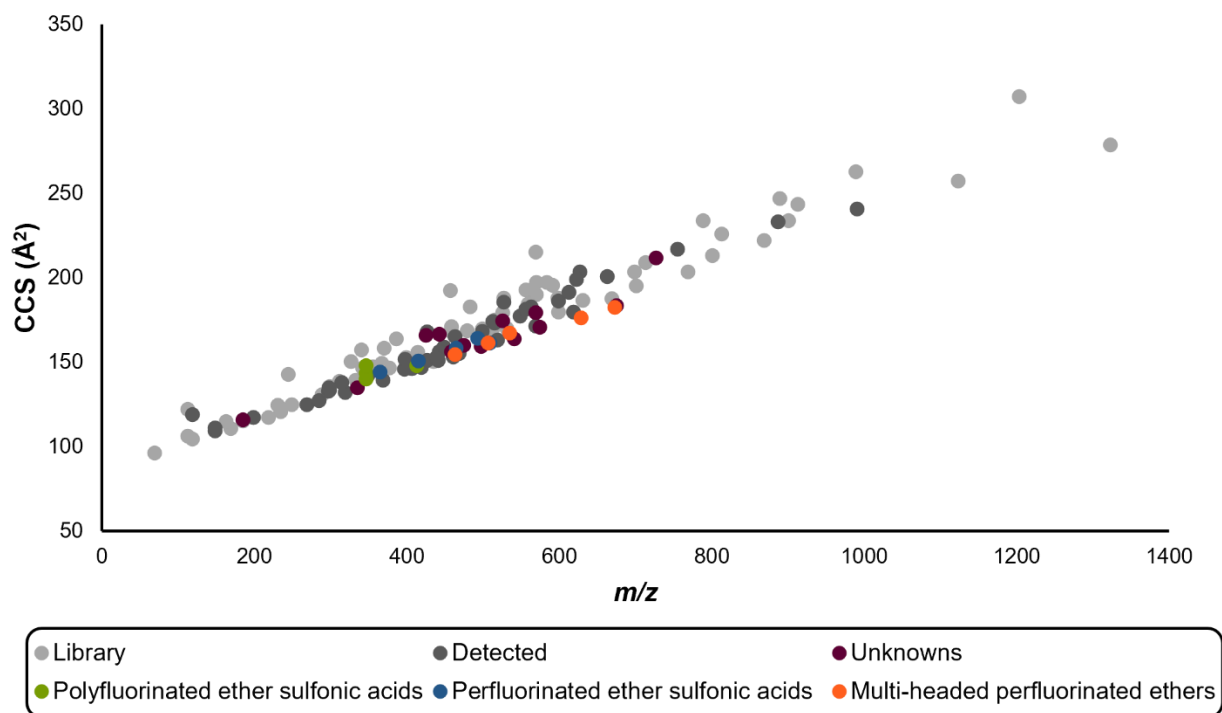
**Fig. S2.**

Drift time dependent CE ramp from 15-40 ms. The square point and “error bars” indicate the optimal CE value and acceptable CE range for each standard tested.



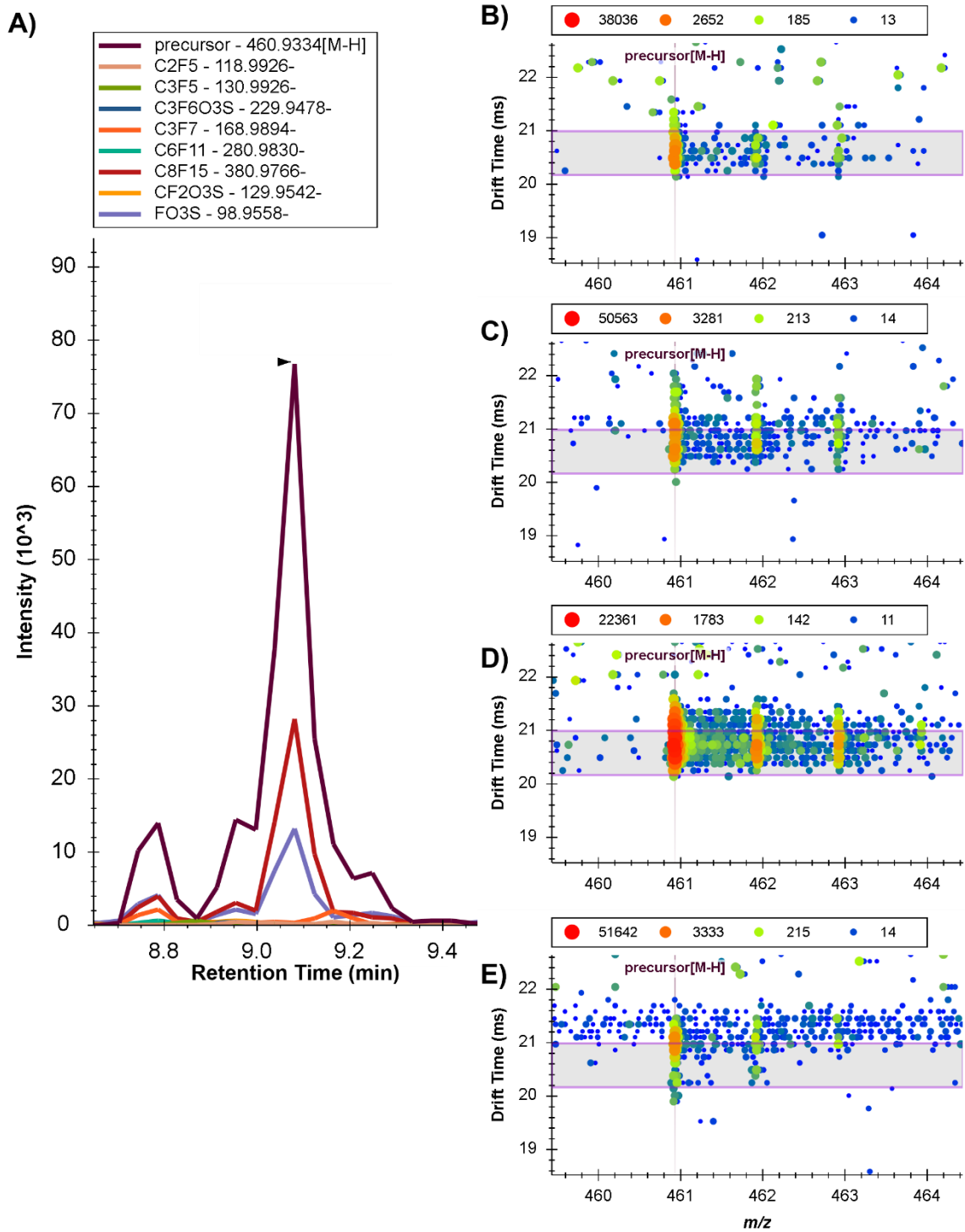
**Fig. S3.**

Extracted ion chromatogram for 6:2 FTS precursor and fragment ions in plant material extract.



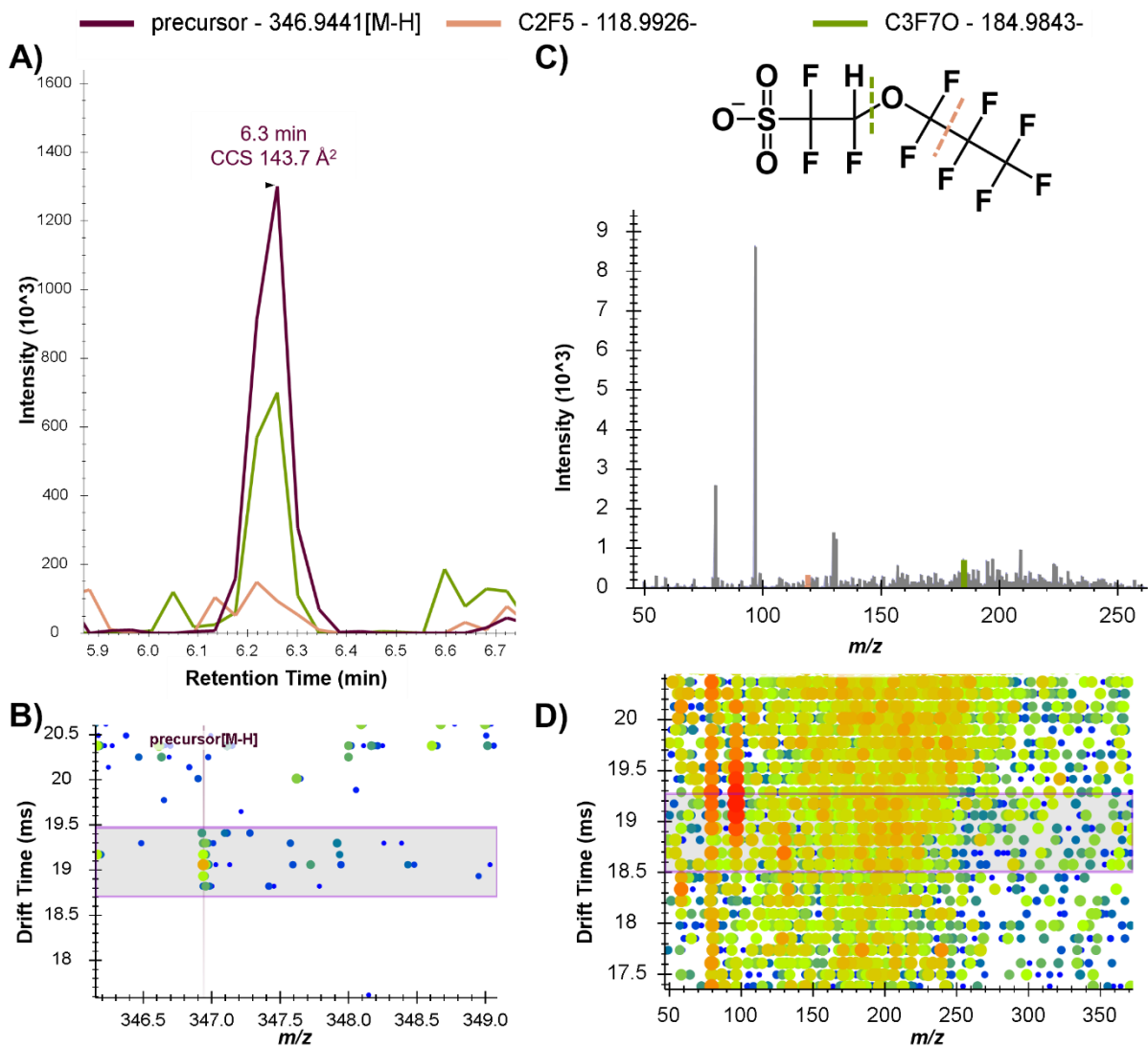
**Fig. S4.**

Collision cross section versus mass-to-charge ratios of PFAS. Gray compounds are known PFAS from the LC-IMS-MS targeted PFAS library that were either detected (dark gray) or not detected (light gray) in the aquatic passive samplers. Colored compounds are unknown features that were either not identified (purple) or were assigned proposed structures (green, blue and orange).



**Fig. S5.**

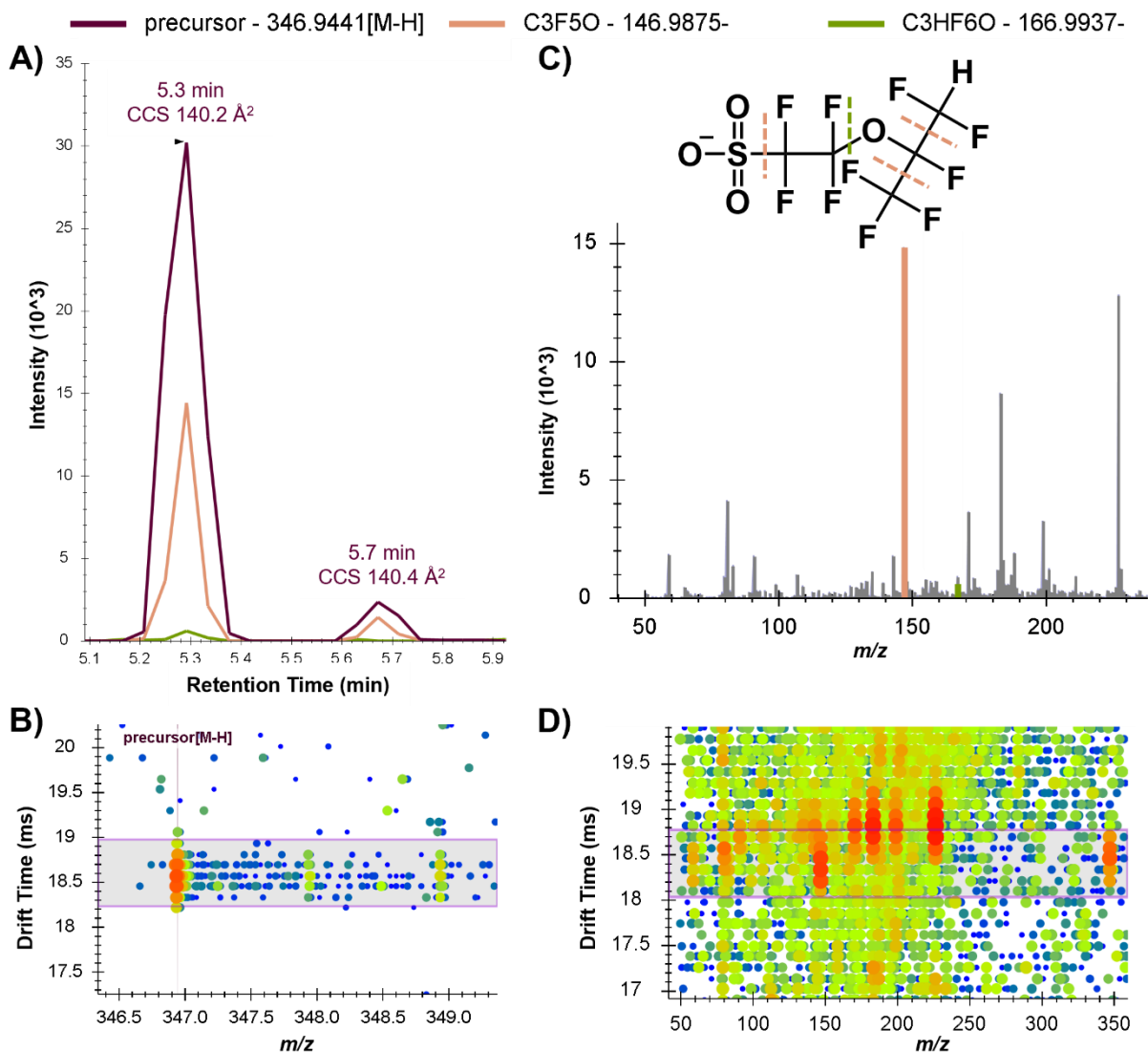
U-PFOS LC-IMS-CID-MS data. (A) Extracted ion chromatogram for the precursor and eight observed fragment ions. Precursor IMS-MS abundance maps at (B) 8.8 min, (C) 8.9 min, (D) 9.1 min, and (E) 9.2 min with drift time filtering windows set by the known PFECHS CCS of 153.3 Å<sup>2</sup>.



**Fig. S6.**

Compound 1 LC-IMS-CID-MS data. **(A)** Extracted ion chromatogram for the precursor and two fragment ions. Two isomers with different CCS values and fragments were proposed to be compound 2. **(B)** Precursor IMS-MS abundance map. **(C)** MS/MS spectrum with annotated fragments. **(D)** IMS-MS/MS abundance map displaying partially interfering fragments from a co-eluting ion at a higher drift time.

Note: Nonspecific sulfonate fragments were not annotated here but were detected.



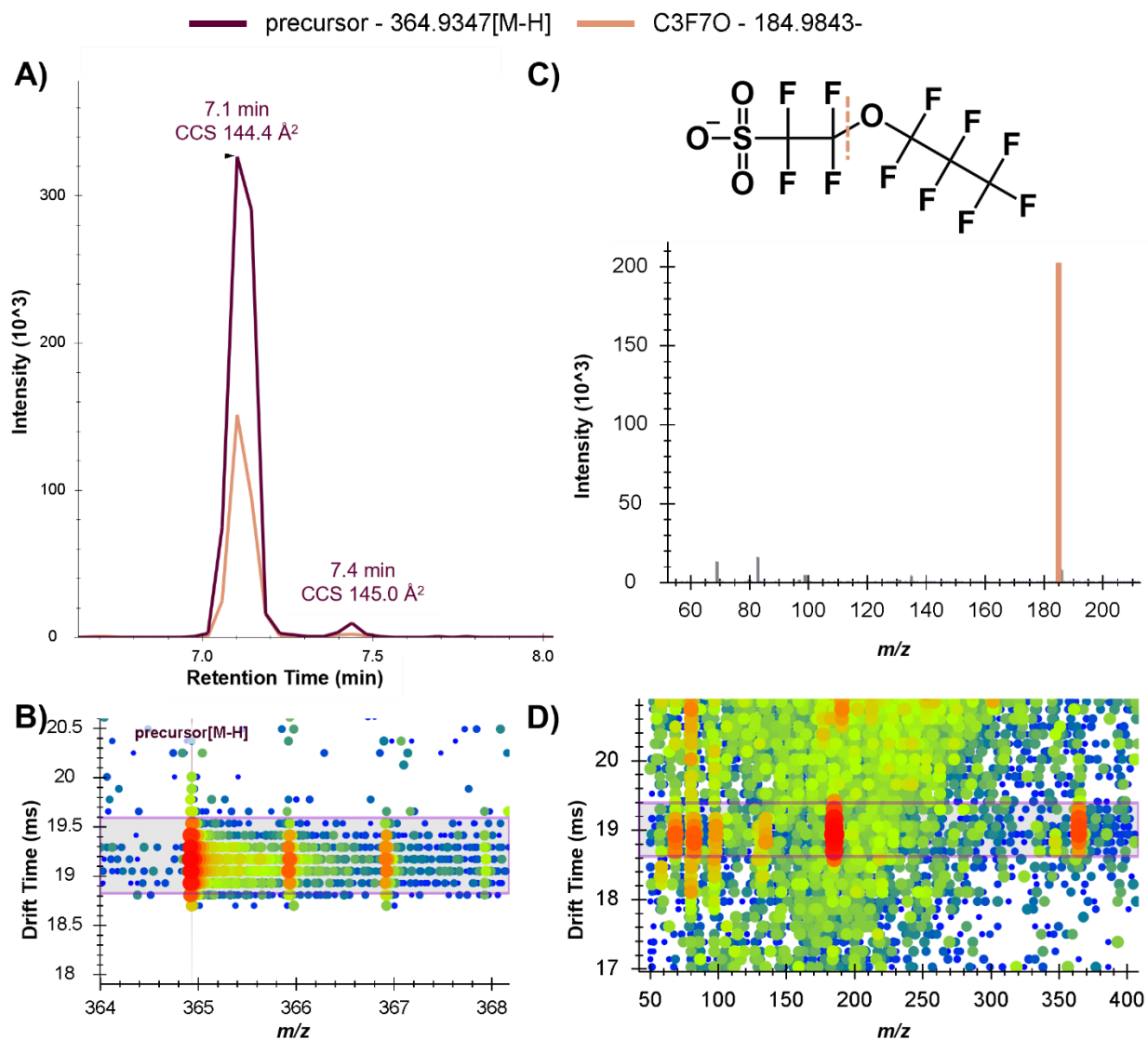
**Fig. S7.**

Compound 2 LC-IMS-CID-MS data. **(A)** Extracted ion chromatogram for the precursor and two fragment ions. Two potential isomers were detected at 5.3 and 5.7 minutes with similar CCS and fragments. A third isomer with dissimilar CCS and fragments was determined to be compound 1. **(B)** Precursor IMS-MS abundance map. **(C)** MS/MS spectrum with annotated fragments. **(D)** IMS-MS/MS abundance map displaying partially interfering fragments from a co-eluting ion at a higher drift time.

Note: Nonspecific sulfonate fragments were not annotated here but were detected.



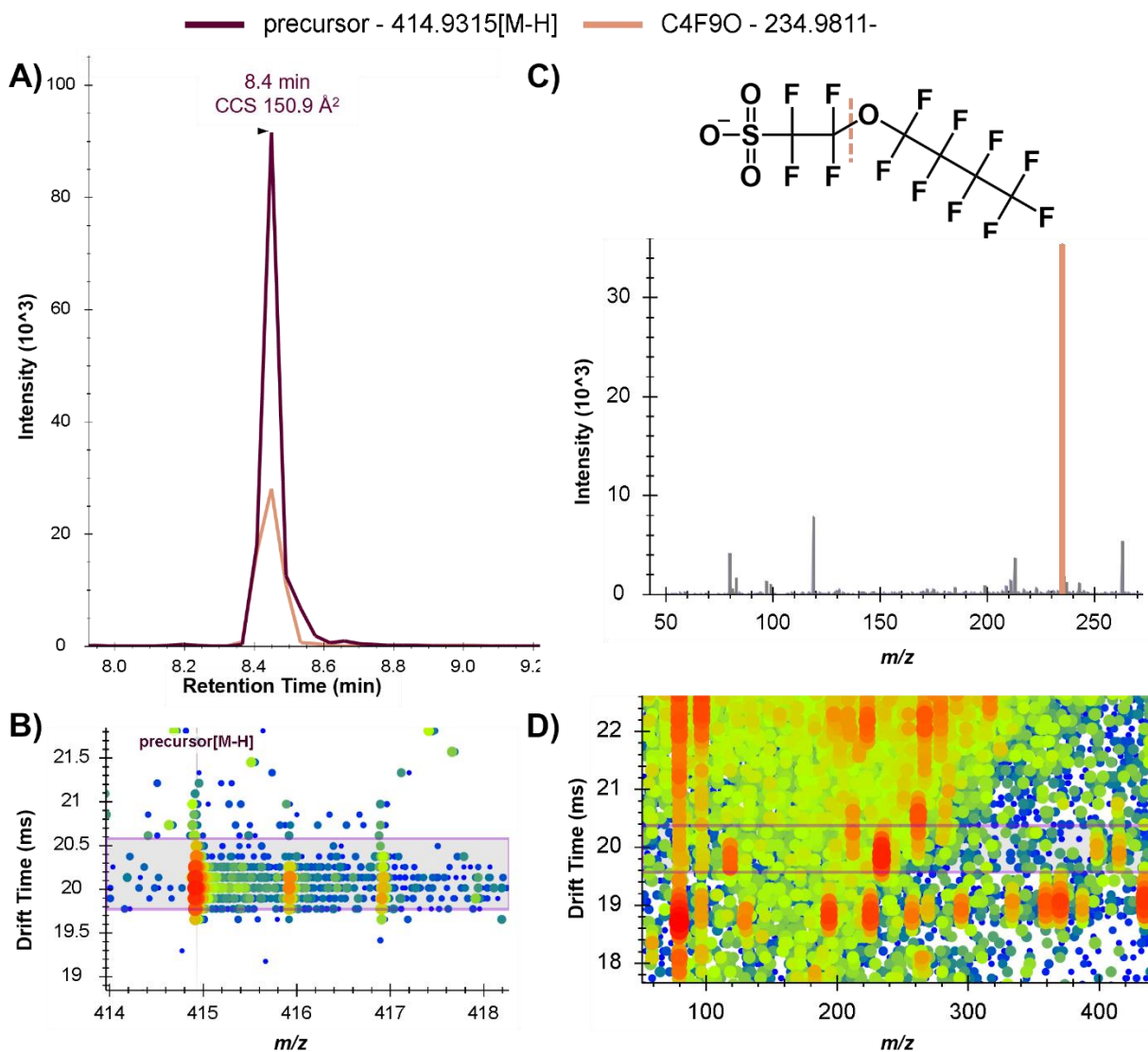




**Fig. S9.**

Compound 4 LC-IMS-CID-MS data. **(A)** Extracted ion chromatogram for the precursor and fragment ion. Two potential isomers were detected at 7.1 and 7.4 minutes with similar CCS and fragments. **(B)** Precursor IMS-MS abundance map. **(C)** MS/MS spectrum with an annotated fragment. **(D)** IMS-MS/MS abundance map.

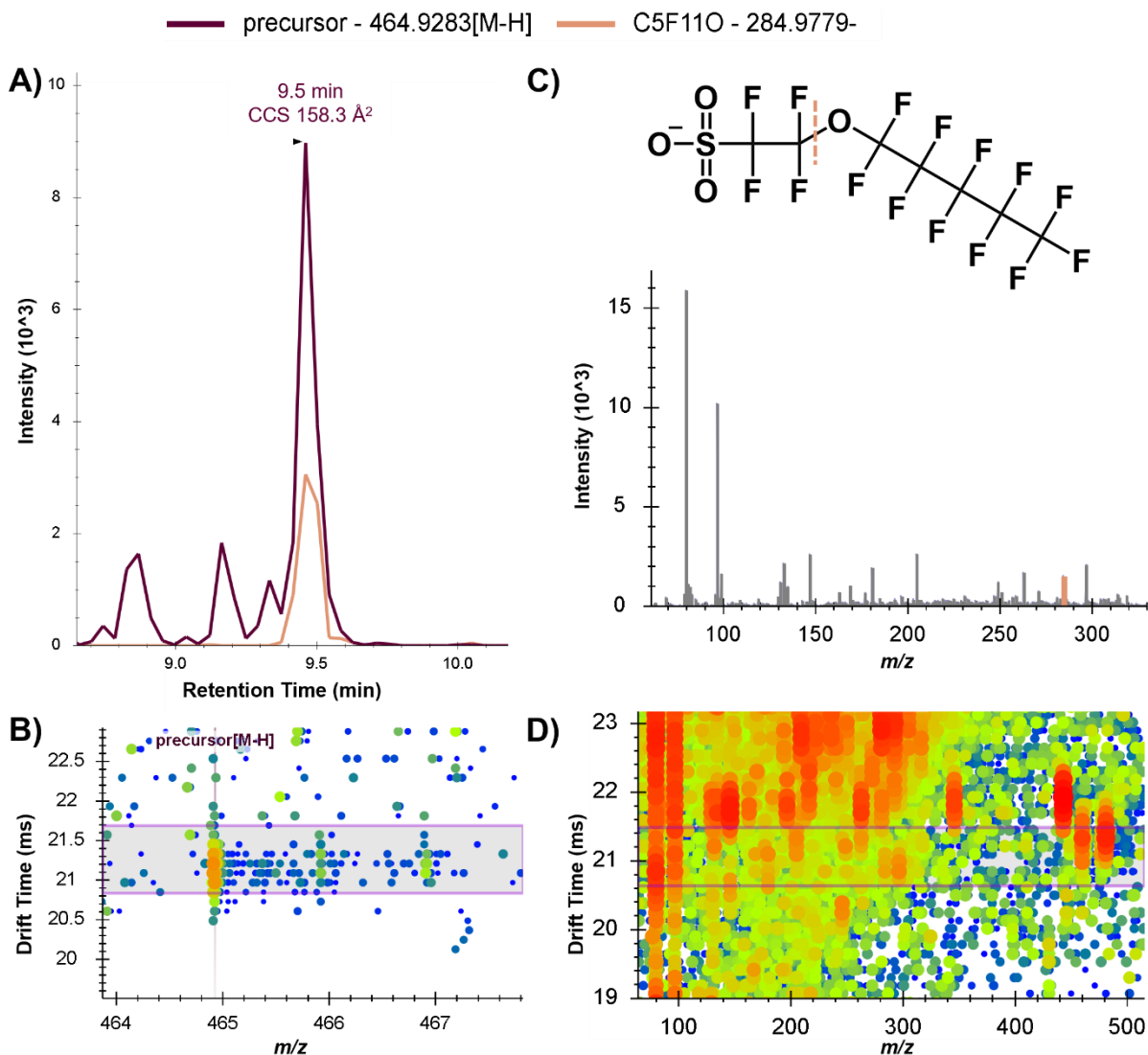
Note: Nonspecific sulfonate fragments were not annotated here but were detected.



**Fig. S10.**

Compound 5 LC-IMS-CID-MS data. (A) Extracted ion chromatogram for the precursor and fragment ion. (B) Precursor IMS-MS abundance map. (C) MS/MS spectrum with an annotated fragment. (D) IMS-MS/MS abundance map displaying partially interfering fragments from a co-eluting ion at a higher drift time.

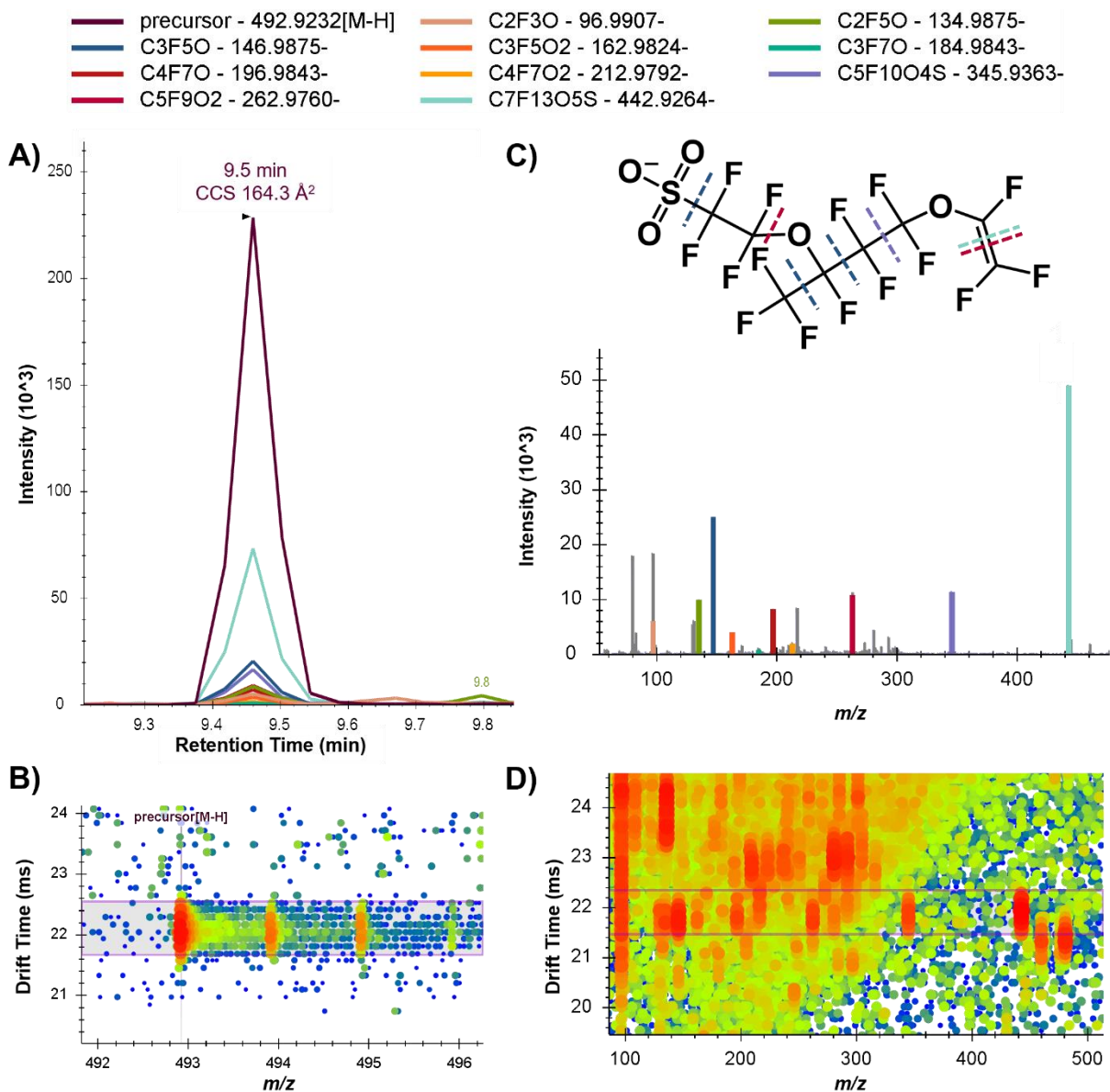
Note: Nonspecific sulfonate fragments were not annotated here but were detected.



**Fig. S11.**

Compound 6 LC-IMS-CID-MS data. **(A)** Extracted ion chromatogram for the precursor and fragment ion. **(B)** Precursor IMS-MS abundance map. **(C)** MS/MS spectrum with an annotated fragment. **(D)** IMS-MS/MS abundance map displaying interfering fragments from a co-eluting ion at higher and lower drift times.

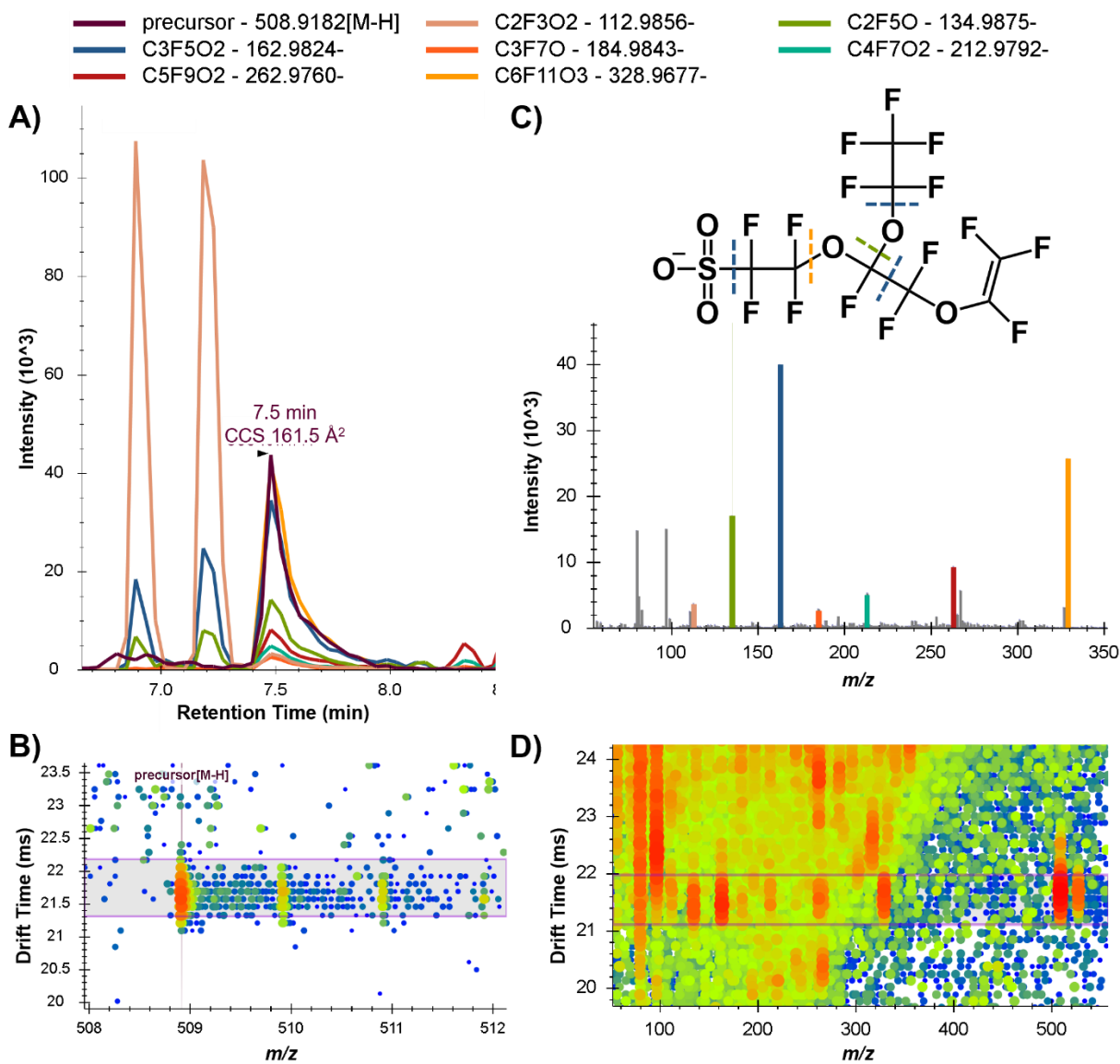
Note: Nonspecific sulfonate fragments were not annotated here but were detected.



**Fig. S12.**

Compound 7 LC-IMS-CID-MS data. **(A)** Extracted ion chromatogram for the precursor and 10 fragment ions. **(B)** Precursor IMS-MS abundance map. **(C)** MS/MS spectrum with three diagnostic fragments annotated. **(D)** IMS-MS/MS abundance map.

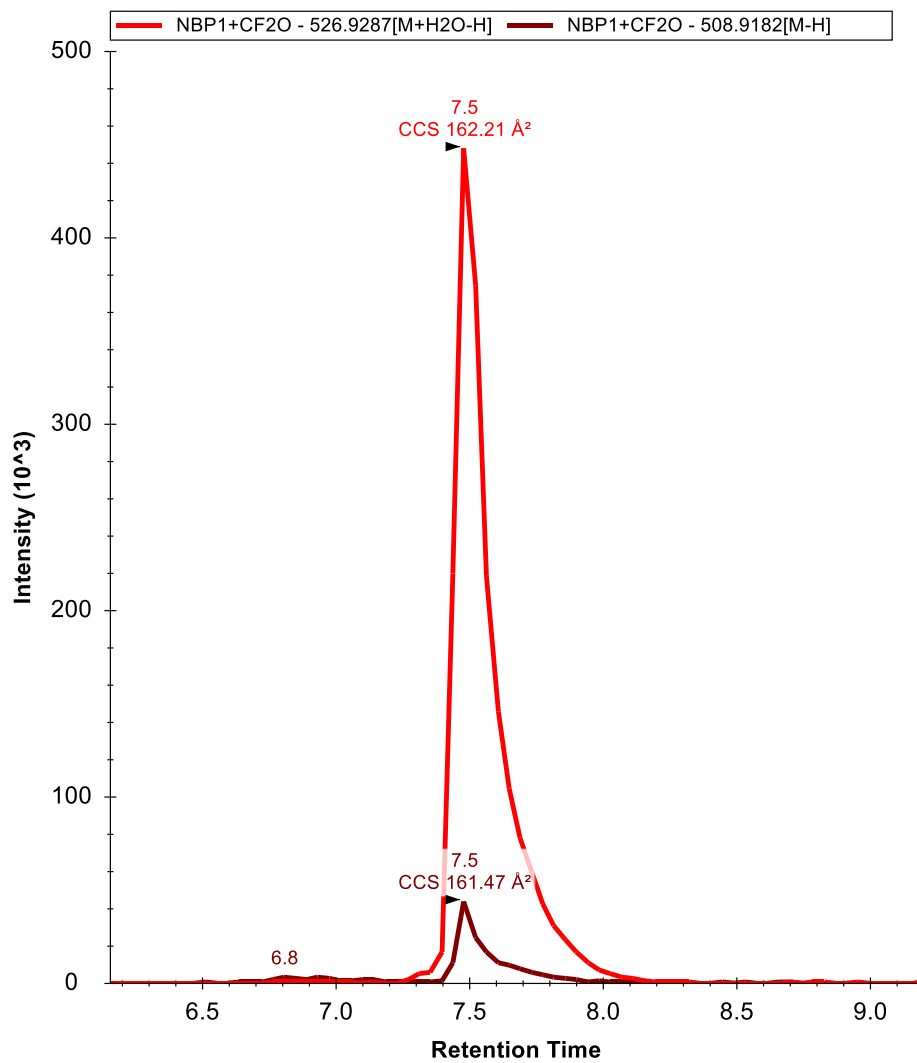
Note: Nonspecific sulfonate fragments were not annotated here but were detected.



**Fig. S13.**

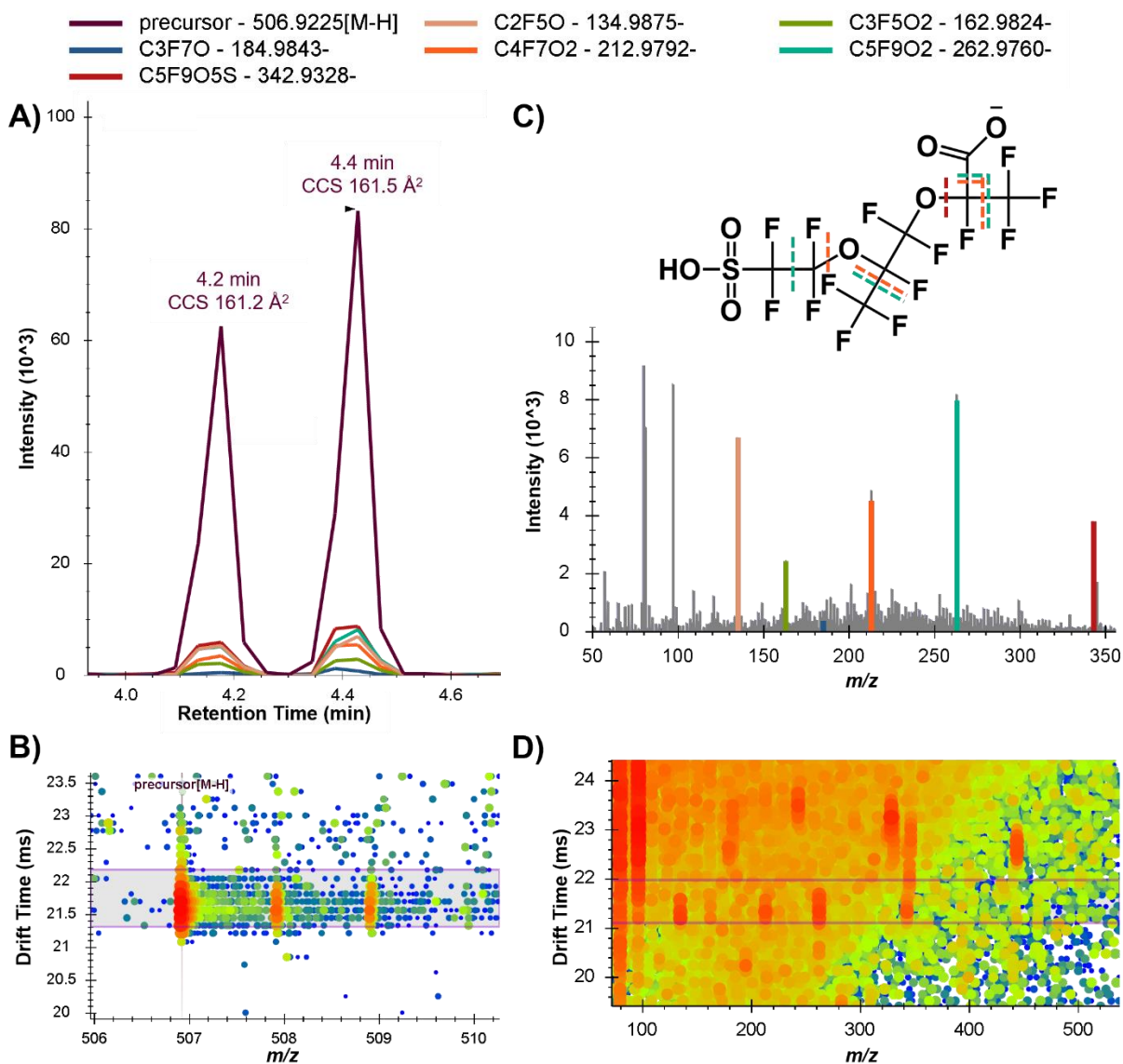
Compound 8 LC-IMS-CID-MS data. **(A)** Extracted ion chromatogram for the deprotonated precursor and 7 fragment ions. The neighboring peaks are fragment ion signals from other precursors with similar CCS values and shared fragments. **(B)** Precursor IMS-MS abundance map. **(C)** MS/MS spectrum with three diagnostic fragments annotated. **(D)** IMS-MS/MS abundance map.

Note: Nonspecific sulfonate fragments were not annotated here but were detected.



**Fig. S14.**

Overlaid extracted ion chromatograms for the [M-H]<sup>-</sup> and [M+H<sub>2</sub>O-H]<sup>-</sup> adducts of compound 8.

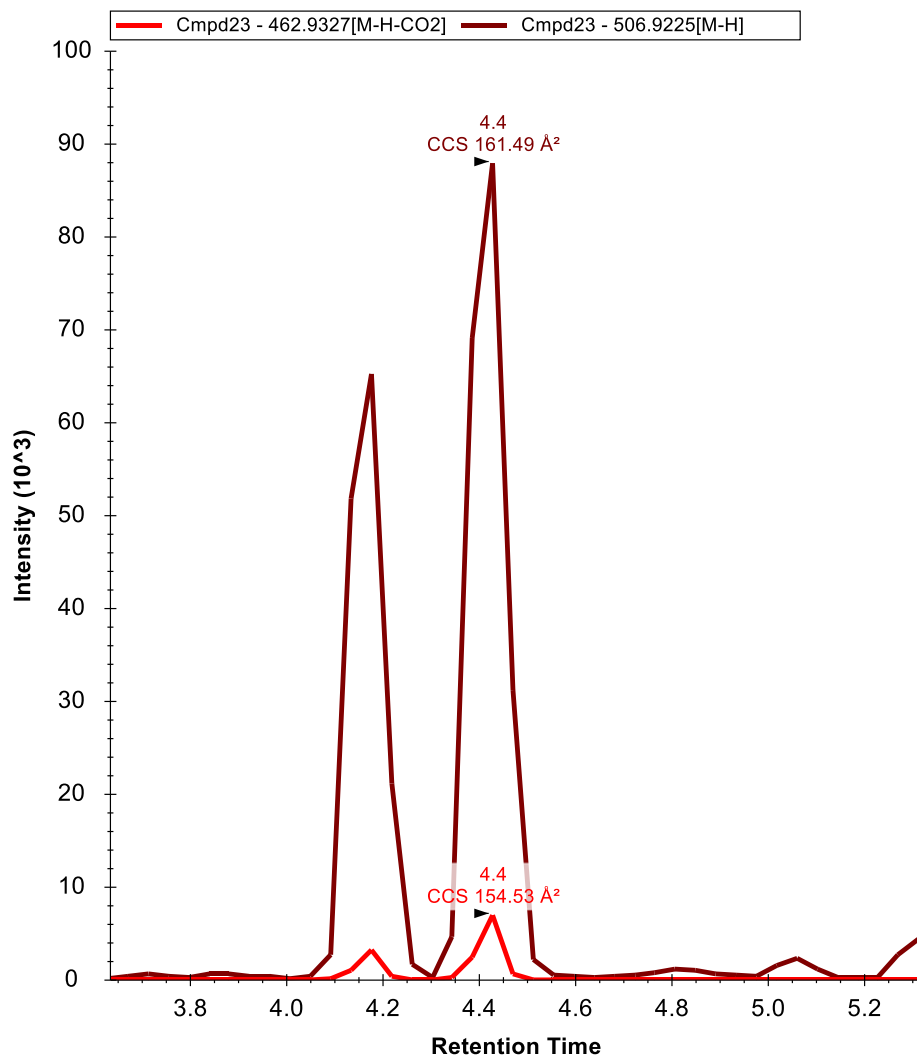


**Fig. S15.**

Compound 9 LC-IMS-CID-MS data. **(A)** Extracted ion chromatogram for the deprotonated precursor and 6 fragment ions. Two potential isomers were detected at 4.2 and 4.4 minutes with similar CCS and fragments. **(B)** Precursor IMS-MS abundance map. **(C)** MS/MS spectrum with three diagnostic fragments annotated. **(D)** IMS-MS/MS abundance map.

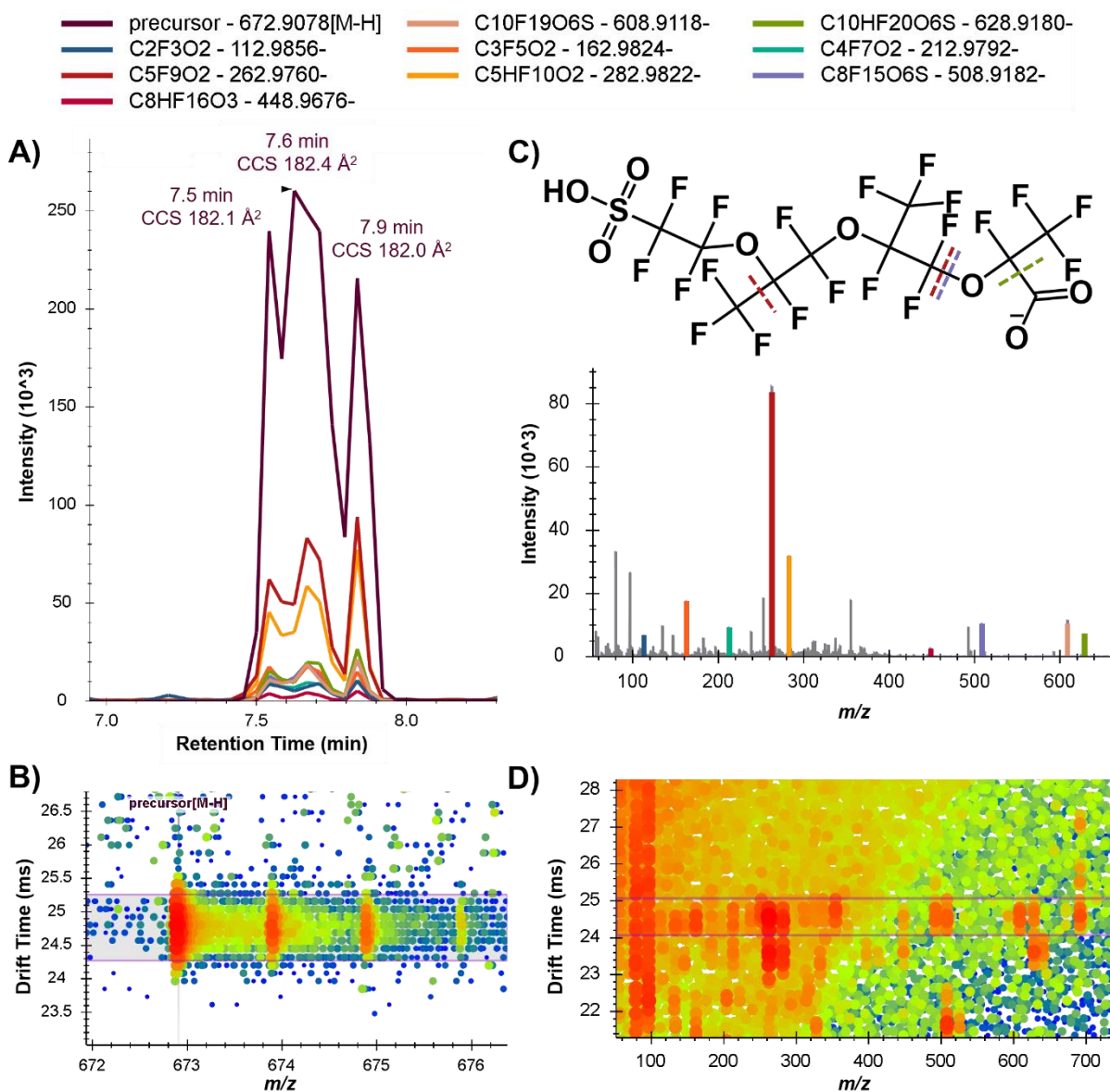
Note: Nonspecific sulfonate fragments were not annotated here but were detected.





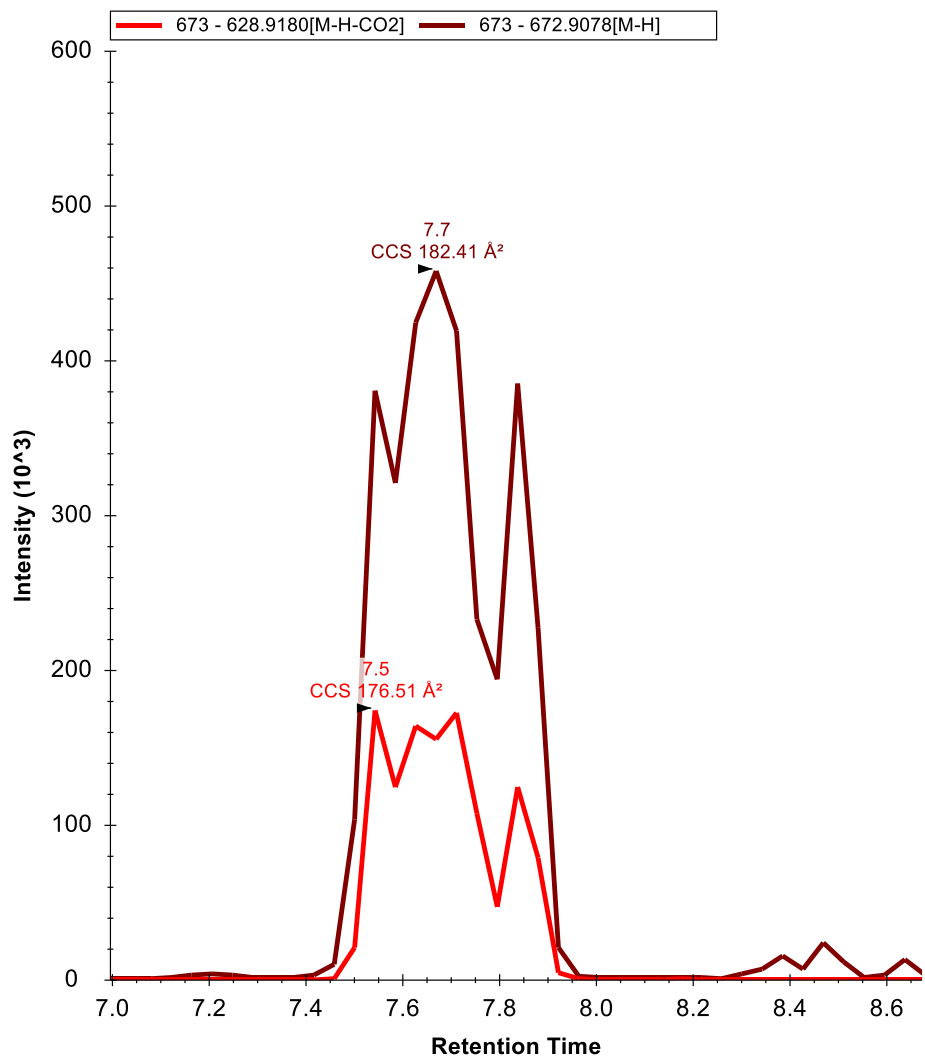
**Fig. S16.**

Overlaid extracted ion chromatograms for the  $[M-H]^-$  and  $[M-H-CO_2]^-$  adducts of compound 9.



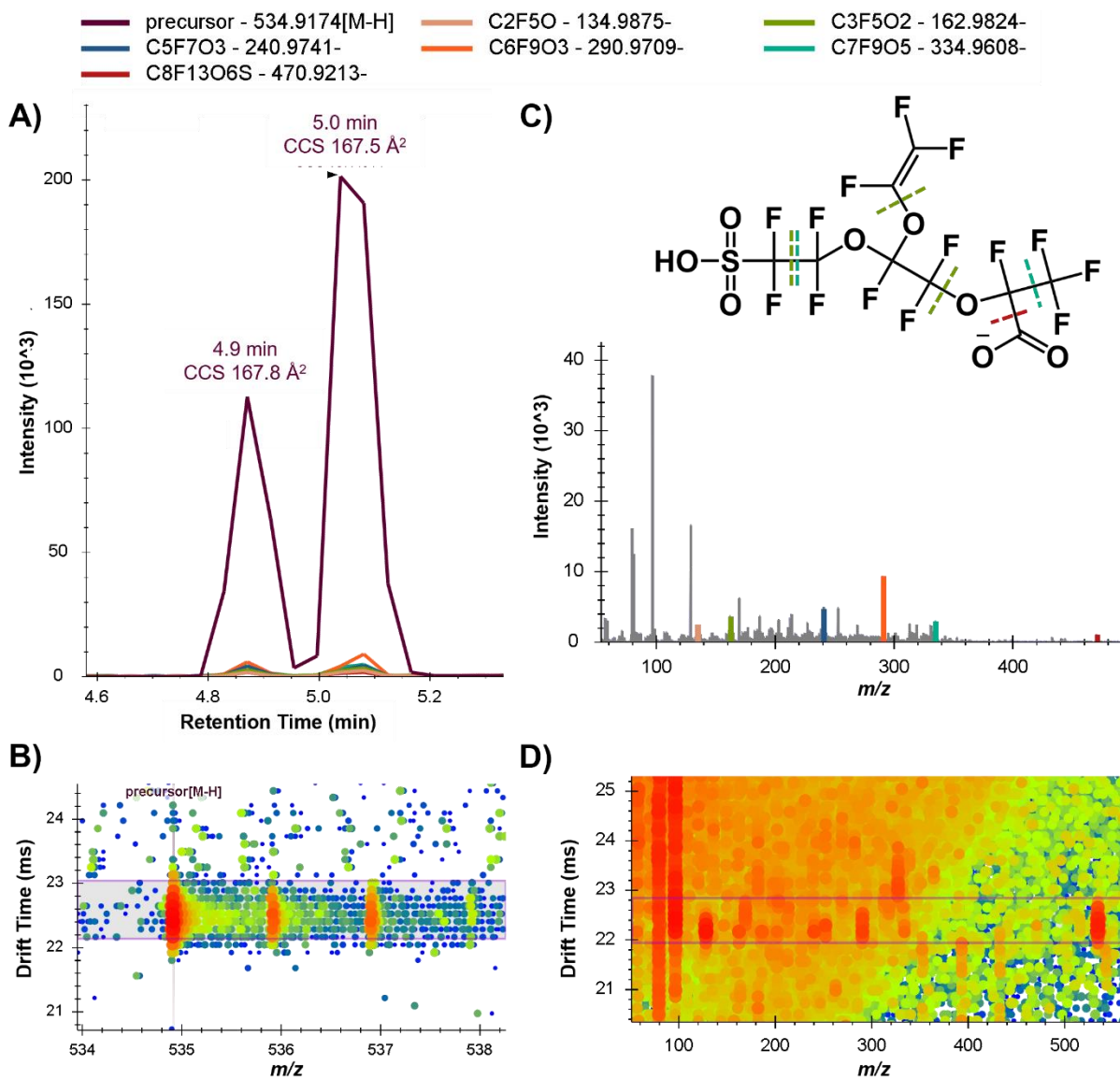
**Fig. S17.**

Compound 10 LC-IMS-CID-MS data. **(A)** Extracted ion chromatogram for the deprotonated precursor and 9 fragment ions. At least three potential unresolved isomers were detected at 7.5, 7.6 and 7.9 minutes with similar CCS and fragments. **(B)** Precursor IMS-MS abundance map. **(C)** MS/MS spectrum with three diagnostic fragments annotated. **(D)** IMS-MS/MS abundance map. Note: Nonspecific sulfonate fragments were not annotated here but were detected.



**Fig. S18.**

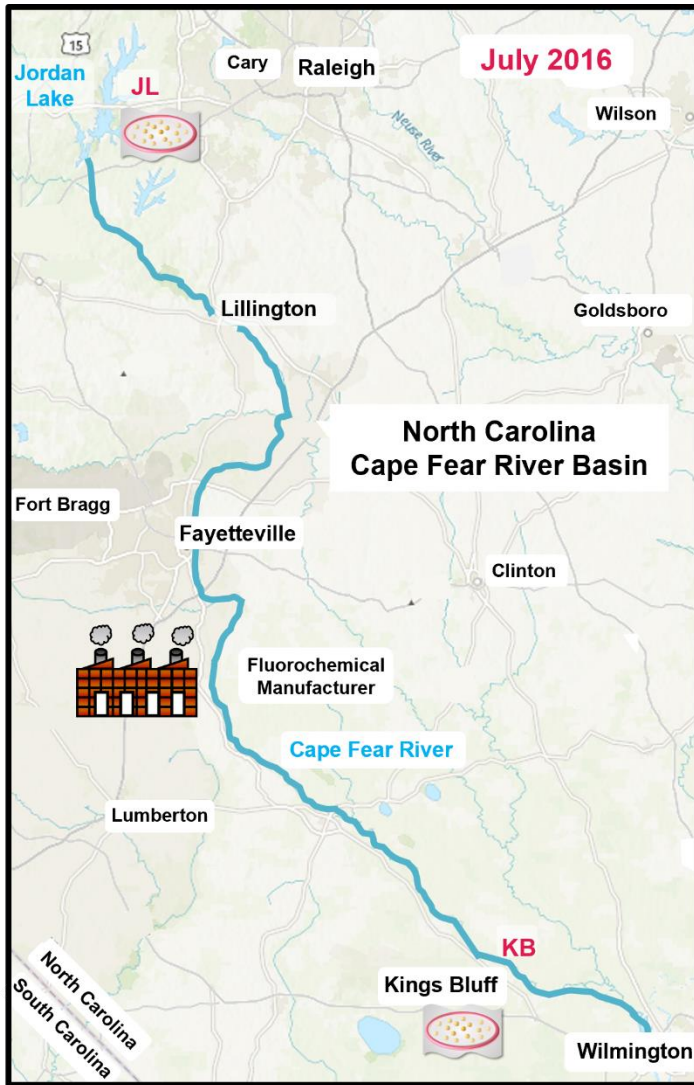
Overlaid extracted ion chromatograms for the  $[M-H]^-$  and  $[M-H-CO_2]^-$  adducts of compound 10.



**Fig. S19.**

Compound 11 LC-IMS-CID-MS data. **(A)** Extracted ion chromatogram for the deprotonated precursor and 6 fragment ions. Two potential isomers were detected at 4.9 and 5.0 minutes with similar CCS and fragments. **(B)** Precursor IMS-MS abundance map. **(C)** MS/MS spectrum with three diagnostic fragments annotated. **(D)** IMS-MS/MS abundance map.

Note: Nonspecific sulfonate fragments were not annotated here but were detected.



**Fig. S20.**

Map of aquatic passive sampler deployment locations. The control body of water, Jordan Lake (JL), and contaminated body of water, the Kings Bluff (KB) region of the Cape Fear River, are labeled.

Name	Confidence	Formula	RT (min)	CCS (Å <sup>2</sup> )	m/z	CAS
PFDS	1a	C10HF21O3S	11.8	186.21	598.9238	335-77-3
PFNS	1a	C9HF19SO3	11.1	177.24	548.9270	68259-12-1
PFOS	1a	C8HF17O3S	10.1	168.27	498.9302	1763-23-1
PFHpS	1a	C7HF15O3S	9.2	159.24	448.9334	375-92-8
PFHxS	1a	C6HF13O3S	8.4	150.51	398.9366	355-46-4
PFPeS	1a	C5HF11O3S	7.0	142.20	348.9398	2706-91-4
PFBS	1a	C4HF9O3S	5.2	133.62	298.9430	375-73-5
8Cl-PFOS	1a	C8HClF16O3S	10.7	173.33	514.9007	1651215-26-7
PFECHS	1a	C8F15HO3S	9.0	153.34	460.9334	335-24-0
PFTTrDA	1a	C13HF25O2	12.9	179.65	618.9606	72629-94-8
PFD <sub>o</sub> A	1a	C12HF23O2	12.4	171.50	568.9638	307-55-1
PFU <sub>d</sub> A	1a	C11HF21O2	11.8	163.36	518.9670	2058-94-8
PFDA	1a	C10HF19O2	11.1	155.28	468.9702	335-76-2
PFNA	1a	C9HF17O2	10.3	147.02	418.9734	375-95-1
PFOA	1a	C8HF15O2	9.4	139.50	368.9766	335-67-1
PFHpA	1a	C7HF13O2	8.2	132.38	318.9798	375-85-9
PFHxA	1a	C6HF11O2	6.7	125.10	268.9830	307-24-4
PFPrA	1a	C3HF5O2	10.5	119.28	118.9920	422-64-0
8:2 FTS	1a	C10H5F17SO3	11.1	185.80	526.9615	39108-34-4
6:2 FTS	1a	C8H5F13SO3	9.3	168.13	426.9679	27619-97-2
HFPO-TA (H <sup>+</sup> dimer)	1a	C18H2F34O8	10.7	240.87	990.9128	13252-14-7
PFO5D <sub>o</sub> A (H <sup>+</sup> dimer)	1a	C14H2F26O14	10.2	233.35	886.8951	39492-91-6
PFO4DA (H <sup>+</sup> dimer)	1a	C12H2F22O12	8.9	217.05	754.9117	39492-90-5
PFO3OA (H <sup>+</sup> dimer)	1a	C10H2F18O10	6.9	198.95	622.9282	39492-89-2
Hydro-EVE	1a	C8H2F14O4	8.3	151.20	426.9651	773804-62-9
HFPO-DA (GenX)*	1a	C6HF11O3	7.1	127.46	284.9779	13252-13-6
Nafion byproduct 1	1a	C7HF13O5S	9.1	156.20	442.9264	29311-67-9
Nafion byproduct 2	1a	C7H2F14O5S	8.5	155.21	462.9327	749836-20-2
Nafion byproduct 4	1a	C7H2F12O6S	2.8	151.27	440.9308	

Nafion byproduct 5	1a	C7H3F11O7S	3.0	152.91	438.9351	
Nafion byproduct 6	1a	C6H2F12O4S	8.5	146.16	396.9409	
PFEESA	1a	C4HF9O4S	6.3	137.99	314.9379	113507-82-7
NVHOS	1a	C4H2F8O4S	3.4	132.93	296.9473	801209-99-4
FOSAA	1a	C10H4F17NO4S	10.5	181.66	555.9517	2806-24-8
FHxSA	1a	C6H2F13SO2N	9.8	151.96	397.9526	41997-13-1
FBSA	1a	C4H2F9SO2N	6.7	134.99	297.9590	30334-69-1
Compound 1	2a	C5H2F10O4S	6.3	143.73	346.9441	935443-55-3
Compound 2	2b	C5H2F10O4S	5.3	140.15	346.9441	
Compound 3	2b	C6H2F12O5S	7.3	148.21	412.9359	
Compound 4 (PFPrESA)	2a	C5HF11O4S	7.1	144.36	364.9347	
Compound 5 (PFBESA)	2b	C6HF13O4S	8.4	150.85	414.9315	
Compound 6 (PFPeESA)	2b	C7HF15O4S	9.5	158.32	464.9283	
Compound 7	2b	C8HF15O5S	9.5	164.26	492.9232	
Compound 8	3b	C8HF15O6S	7.5	162.21	526.9287	
Compound 9	2a	C8H2F14O7S	4.4	154.53	462.9327	1235024-21-1
Compound 10	3b	C11H2F20O8S	7.7	182.41	672.9078	
Compound 11	3b	C9H2F14O8S	5.0	197.45	534.9174	
Unknown 1	4	C8H2F13O3S	9.3	165.86	424.9484	
Unknown 2	4	C8H3F16O4S	7.3	159.53	497.9424	
Unknown 3	4	C9H2F16O6S	5.4	163.87	540.9244	
Unknown 4	4	C9H4F16O8S	8.5	170.69	574.9299	

Unknown 5	n/a	5b	10.6	116.1	184.9843	
Unknown 6	n/a	5b	10.6	134.96	334.9747	
Unknown 7	n/a	5b	7.6	156.21	458.9555	
Unknown 8	n/a	5b	6.9	160.01	474.9491	
Unknown 9	n/a	5b	5	174.59	525.9392	
Unknown 10	n/a	5b	5.3	179.55	568.9573	

**Table S1.**

Detected known and unknown PFAS. Identification confidence scores are assigned based on the framework from Charbonnet *et al.*(62)

\*Observed as decarboxylated ion rather than deprotonated. Reported  $m/z$  corresponds to the detected ion ( $[M-H-CO_2]^-$ ).



<b>Name</b>	<b>Formula</b>	<b>ID(24)</b>	<b>Agreement</b>
HFPO-DA (GenX)	C6HF11O3	7	Same structure assigned
Nafion byproduct 1	C7HF13O5S	16	Same structure assigned
Nafion byproduct 2	C7H2F14O5S	34	Same structure assigned
Nafion byproduct 4	C7H2F12O6S	22	Same structure assigned
Nafion byproduct 5	C7H3F11O7S	21	Same structure assigned
Nafion byproduct 6	C6H2F12O4S	28	Same structure assigned
PFO4DA	C6HF11O6	10	Same structure assigned
PFO3OA	C5HF9O5	6	Same structure assigned
Hydro-EVE	C8H2F14O4	29	Same structure assigned
NVHOS	C4H2F8O4S	26	Same structure assigned
PFEESA	C4HF9O4S	14	Same structure assigned
Compound 1	C5H2F10O4S	27	Same structure assigned
Compound 3	C6H2F12O5S	33	Isomeric structures assigned
Compound 4	C5HF11O4S	15	Same structure assigned
Compound 7	C8HF15O5S	17	Isomeric structures assigned
Compound 9	C8H2F14O7S	23	Same structure assigned
Unknown 3	C9H2F16O6S	35	No structure assigned

**Table S2.**

Comparison of identification overlap between this study and McCord & Strynar.(24)

<b>Parameter</b>	<b>Value</b>	<b>Units</b>
Gas Temperature	230	°C
Drying Gas	11	L/min
Nebulizer	25	psi
Sheath Gas Temperature	350	°C
Sheath Gas Flow	12	L/min
$V_{\text{cap}}$	2000	V
Nozzle Voltage	0	V

**Table S3.**  
Ionization source settings

<b>Parameter</b>	<b>Value</b>	<b>Units</b>
Mass Range	50-1700	<i>m/z</i>
Trap Fill Time	20000	$\mu$ s
Trap Release Time	300	$\mu$ s
Frame Rate	0.9	Frames/s
IM Transient Rate	17	IM Transients/Frame
Max Drift Time	60	ms
TOF Transient Rate	502	Transients/IM Transients
Drift Tube Entrance	-1574	V
Drift Tube Exit	-224	V

**Table S4.**  
IMS-MS settings

<b>Drift Time (ms)</b>	<b>Collision Energy (V)</b>
0	2
10	5
15	19
21	32
25	41
35	53
45	60
60	60

**Table S5.**  
CE ramp settings