PFASt and Furious: A Targeted and Non-Targeted LC-MS/MS Study on the Environmental Impact of Using Fluorinated Ski Waxes

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INTRODUCTION

Perfluoroalkyl substances (PFAS) are known to have been commonly used in ski wax formulations. While regulations are changing for the manufacture of ski wax to exclude PFAS, the persistence of this class of compounds means they could still be detected for years. Given the hazards and global concern about PFAS contamination, this study investigated if the contamination could be detected in water and soil samples collected at local slalom and cross-country racing ski sites. This study used both targeted tandem quadrupole and non-targeted high-resolution mass spectrometry (HRMS) with ion mobility to detect and quantify known PFAS in water and soil, as well as investigate new and unexpected PFAS.

METHODS

Sample Preparation

Water and soil samples were collected from a variety of locations on a downhill slalom ski slope as well as along a nordic cross country ski track, both in New England. Sample analysis followed similar protocols provided by US EPA method 1633A.[1]

Soil samples were extracted using the CEM EDGE automated pressurized fluid extraction system. Using this method, sample extraction time was < 10 minutes per sample.

Extracted soil samples and water samples were cleaned up using the Promochrom SPE-03 automated SPE system. High capacity inline filters were fitted to each sample to filter particulates and prevent clogging. Oasis™ WAX/GCB for PFAS Analysis SPE Cartridges were used on the SPE system. Cartridges with GCB on top were used for the soil samples and GCB on the bottom for water samples. The system can run 8 samples in one batch. For the soil samples (50 mL) a batch can be completed in approximately 1 hour, and for water samples (250 mL) a batch was completed in approximately 2 hours.

LC-MS/MS Conditions

LC System: ACQUITY™ Premier System with BSM, FTN and fitted with PFAS Kit

Isolator Column: Atlantis™ Premier BEH™ C18 AX, 2.1 x 50 mm, 2.5 µm Column

Analytical Column: ACQUITY Premier BEH C18, 2.1 x 50 mm, 1.7 µm Column

Column Temp: 35°C

Sample Temp: 10°C

Injection Volume: 2 µl

Flow Rate: 0.3 mL/min

Mobile Phase A: Water + 2 mM ammonium acetate

Mobile Phase B: Acetonitrile + 2 mM ammonium acetate

Gradient:

Time (min)	%A	%B	Curve
0	95	5	initial
0.5	75	25	6
3	50	50	6
6.5	15	85	6
7	5	95	6
8.5	5	95	6
9	95	5	6
11	95	5	6

MS System: Xevo™ TQ Absolute Mass Spectrometer

Ionization Mode: ESI-

Capillary Voltage: 0.5 kV

Desolvation Temp: 350°C

Desolvation Gas Flow: 900 L/hr

Cone Gas Flow: 150 L/hr

Source Temperature: 100°C

LC-cIMS-HRMS Conditions

LC System: ACQUITY I-Class Plus UPLC™ System fitted with the PFAS Analysis Kit

Isolator Column: Atlantis Premier BEH C18 AX, 2.1 x 50 mm, 2.5 µm Column

Analytical Column: Atlantis Premier BEH™ C18A X, 1.7 µm; 2.1mm x 100 mm

Column Temp: 35°C

Sample Temp: 10°C

Injection Volume: 30 µl

Flow Rate: 0.3 mL/min

Mobile Phase A: Water + 2 mM ammonium acetate

Mobile Phase B: Methanol + 0.1% Ammonium Hydroxide

Gradient:

Time (min)	%A	%B	Curve
0	99	1	initial
2	99	1	6
3	75	25	6
8	50	50	6
15	15	85	6
16	0	100	6
20	0	100	6
20.1	100	0	6
23.5	100	0	6
24	99	1	6

MS System: SELECT SERIES™ Cyclic™ IMS

Ionization Mode: ESI-

Capillary Voltage: 0.5 kV

Cone Voltage: 10 V

MS Analyzer Mode: V Mode (MS Resolution ~60,000 FWHM)

Mass Range: m/z 50-1200

MS Acquisition: DIA HDMSE

Ion Mobility Resolution: ~65 Ω/ΔΩ (Single Pass, FWHM)

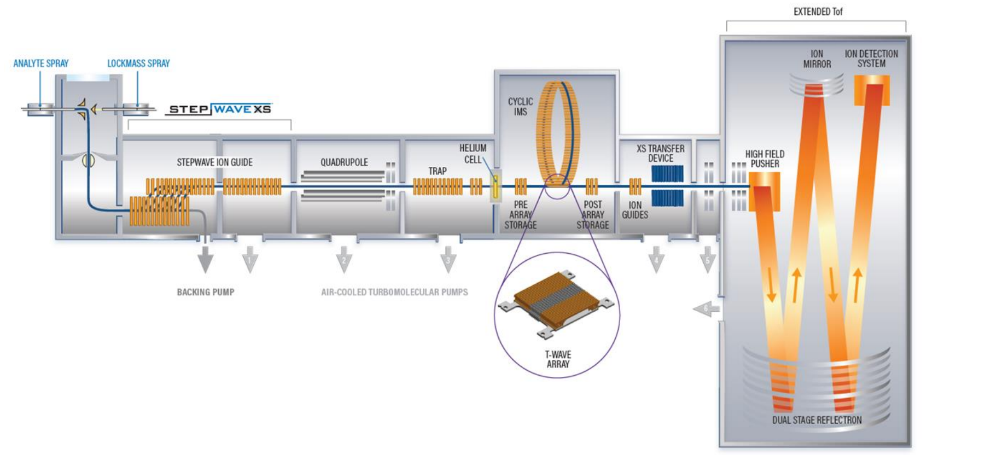


Figure 1. Instrument schematic of the SELECT SERIES Cyclic IMS QTOF.

RESULTS AND DISCUSSION

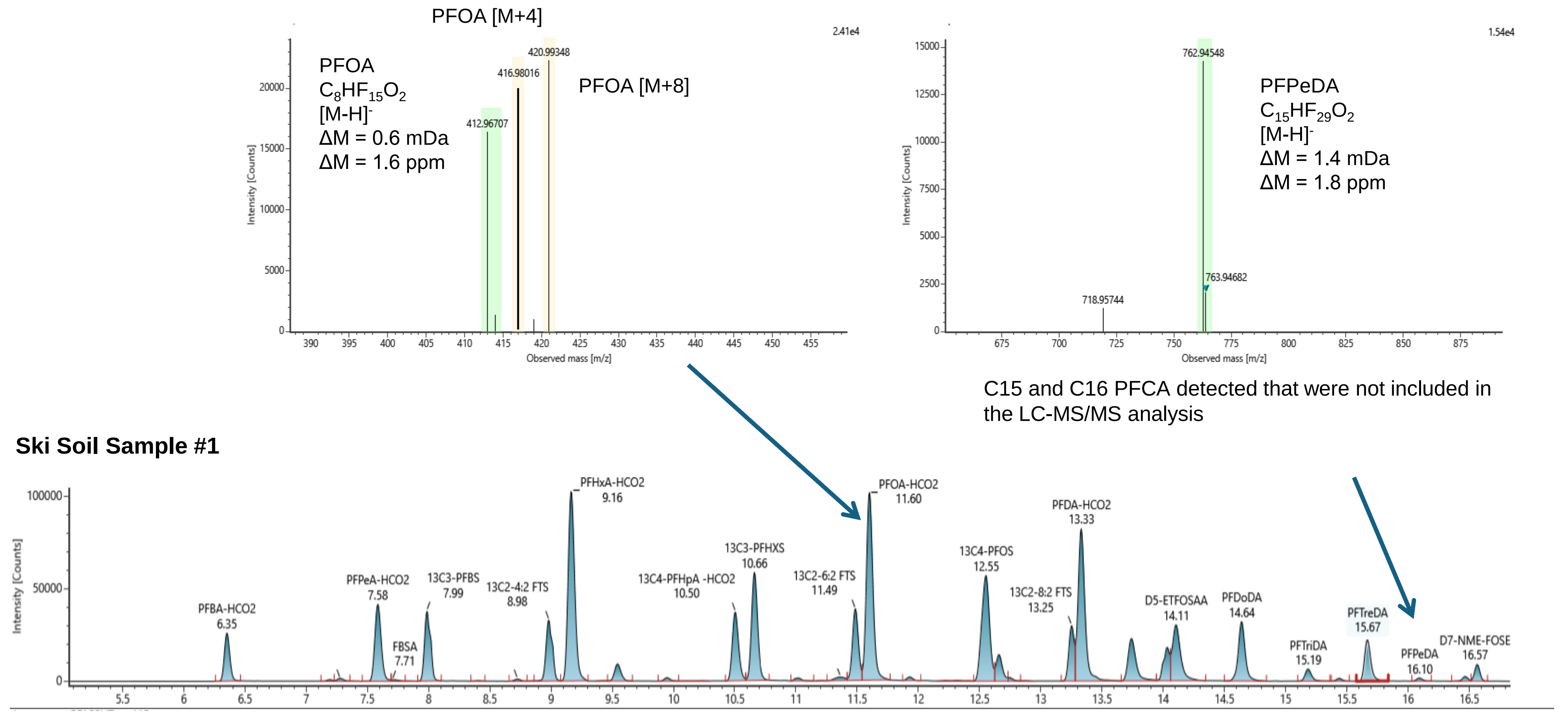
Significant levels of PFAS were detected and quantified at both the slalom racing and cross-country racing ski sites. Carboxylic acids made up the majority of the PFAS detected in all samples from both locations, more specifically the longer chain carboxylates, which are what are predominantly used in ski wax formulations. Tables 1 and 2 show the PFAS detected at the slalom racing site and cross-country ski site, respectively. The values are represented in parts per trillion (ppt) for both water and soil to demonstrate the levels in soil are significantly higher than in the water collected at each site. At the slalom racing site, there is a clear trend of PFAS levels decreasing as the sampling site moves down the ski slope, which correlates with the ski wax abrading off the skis as they are used. At the cross-country ski track, PFAS are found at various levels along the entire racing track, but are highest where the ski wax is being applied and skis are tested (wax testing hill and parking lot). Additionally, there are significantly high levels in the ponds surrounded by the course as well as an on-site vegetable garden, indicating that the PFAS contamination is migrating through the environment at this site, most likely through water run-off from snow melt. There is an extremely high (3533 ng/kg) detection of PFOS in the garden as well, which does not look to be originating from the ski wax contamination and needs further investigation. Ion mobility high resolution mass spectrometry was also used to detect a series of long chain (up to C16) carboxylic acids in the soil samples that were not targeted in the LC-MS/MS analysis. Further data processing is being completed on the non-targeted data collected to look for unknown PFAS compounds in the soil samples. Previous HRMS work has identified the presence of dioic perfluorinated acids and monohydrogen-substituted perfluoroalkyl carboxylic acids at the slalom racing slope, series of PFAS that are not routinely included in any common targeted analysis workflows for PFAS analysis.[2]

Down Slope → Down Slope →

	Soil (ng/kg)				Surface Water (ng/L)				
	Wax Station	Start Line	Mid Slope	Finish Line	Wax Station	Start Line	Mid Slope	Finish Line	Retention Pond
PFBA	35	1358	765	407	0.93	1.37	0.75	1.25	1.16
PFPeA	61	520	213	123	0.85	1.22	0.66	0.76	0.65
PFHxA	143	182	135	92	0.40	0.52	0.17	0.42	0.34
PFHpA	153	187	99	106	0.60	0.94	0.08	0.90	0.21
PFOA	248	236	134	124	1.05	1.74	0.23	1.21	0.44
PFNA	183	171	17	7	0.47	0.85	0.11	0.40	0.12
PFDA	284	102	51	23	1.09	0.49	ND	0.42	ND
PFUnDA	218	55	22	5	1.24	0.16	0.06	0.17	ND
PFDoDA	189	63	36	31	1.04	0.08	ND	0.08	ND
PFTriDA	152	45	4	11	0.66	ND	ND	ND	ND
PFTreDA	231	48	10	ND	0.95	ND	ND	ND	ND
PFBS	13	14	5	8	0.24	0.08	0.12	0.42	0.27
PFPeS	ND	ND	ND	ND	ND	ND	ND	ND	ND
PFHxS	BLoQ	BLoQ	9	ND	ND	ND	0.09	0.12	ND
PFHpS	ND	ND	ND	ND	ND	ND	ND	ND	ND
PFOS	45	76	62	18	0.51	0.53	0.21	0.63	0.24
PFNS	ND	ND	ND	ND	ND	ND	ND	ND	ND
PFDS	ND	18	38	ND	ND	ND	ND	ND	ND
PFDoDS	ND	ND	ND	ND	ND	ND	ND	ND	ND
6:2 FTS	BLoQ	ND	4	ND	2.65	ND	ND	3.11	ND
NMeFOSA	16	16	26	ND	ND	ND	ND	0.09	ND
NEtFOSA	6	8	25	ND	ND	ND	ND	0.08	ND
NMeFOSE	14	20	32	60	ND	0.14	ND	0.56	0.13
NEtFOSE	ND	BLoQ	83	ND	ND	0.17	ND	0.60	0.17
Total PFAS	1990	3116	1770	1013	13	8	2	11	4

Highest Concentration
Lowest Concentration

Table 1. Calculated concentrations of PFAS detected in the soil and water samples collected from the alpine downhill slalom ski slope. ND (not detected).



C15 and C16 PFCA detected that were not included in the LC-MS/MS analysis

Ski Soil Sample #1

Figure 2. High Res Data

	Soil (ng/kg)												Surface Water (ng/L)		
	Race Course Near Pond 1	Pond 1 Sediment	Pond 2 Sediment	Start/Finish Line	Garden Near Pond 2	Garden Near Waxing	Ski Wax Test Hill Top	Ski Wax Test Hill Bottom	Race Course Location 1	Race Course Location 2	Non-Race Trail	Parking Lot Waxing Area	Pond 1	Pond 2	Surface Water Near Garden
PFBA	296	1337	1884	201	280	167	98	123	118	102	782	159	ND	2	1
PFPeA	89	307	581	25	318	157	51	140	41	27	363	98	ND	10	ND
PFHxA	12	ND	15	33	259	141	71	126	ND	ND	ND	17	ND	12	ND
PFHpA	40	23	54	50	197	113	43	146	ND	9	50	62	ND	11	ND
PFOA	45	34	73	97	786	378	82	271	47	7	79	145	ND	45	ND
PFNA	39	10	14	87	435	311	47	328	92	41	43	150	ND	42	ND
PFDA	66	15	20	117	1056	261	78	1839	315	54	59	583	ND	81	ND
PFUnDA	33	28	22	66	272	104	46	991	126	46	51	230	ND	17	ND
PFDoDA	19	83	ND	46	358	65	55	1262	89	17	16	450	ND	7	1
PFTriDA	21	247	10	39	133	49	25	945	94	26	22	221	ND	3	0
PFTreDA	25	693	13	57	224	49	58	1554	138	34	26	796	ND	1	1
PFBS	9	ND	ND	58	6	ND	ND	ND	ND	ND	ND	ND	ND	5	ND
PFHxS	17	ND	9	ND	21	9	15	ND	ND	ND	ND	10	ND	ND	ND
PFHpS	16	ND	ND	ND	19	7	11	ND	ND	ND	ND	8	ND	0	ND
PFOS	131	ND	9	186	3533	1048	276	454	60	29	183	27	ND	22	ND
PFNS	12	ND	ND	ND	11	ND	14	ND	ND	ND	ND	13	ND	ND	ND
FOSA	ND	ND	ND	ND	37	9	11	ND	ND	ND	ND	21	ND	ND	ND
N-MeFOSAA	31	17	ND	31	31	16	57	10	ND	17	ND	ND	ND	ND	ND
N-EtFOSAA	22	ND	ND	23	68	23	31	ND	ND	7	ND	10	ND	ND	0
NMeFOSE	ND	27	25	ND	13	14	9	18	15	41	11	32	ND	ND	ND
NEtFOSE	ND	ND	8	ND	39	10	ND	14	ND	6	ND	ND	ND	ND	ND
4:2 FTS	33	ND	ND	ND	16	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
6:2 FTS	ND	178	174	ND	ND	ND	ND	ND	ND	ND	ND	ND	1	ND	1
8:2 FTS	68	ND	ND	93	38	42	ND	53	ND	ND	44	310	1	ND	ND
5:3 FTCA	9	ND	20	12	14	ND	ND	10	16	12	8	7	ND	ND	ND
7:3 FTCA	ND	11	15	14	26	ND	ND	111	16	ND	11	91	ND	ND	ND
Total PFAS	1034	3010	2946	1233	8190	2972	1078	8396	1167	474	1749	3440	2	257	4

Highest Concentration
Lowest Concentration

Table 2. Calculated concentrations of PFAS detected in the soil and water samples collected from the Nordic cross country ski track. Only the water samples that had detectable levels of PFAS are shown in this table. ND (not detected).

CONCLUSIONS

- **The PFAS impact from the use of ski wax during slalom and cross-country ski racing was studied at two sites that are frequently used for high level competitions and training**
- **At both sites, PFAS were detected in soil and water samples, although the soil was significantly more contaminated with PFAS**
- **Long chain perfluorocarboxylic acids are the predominate PFAS detected in all samples**
- **At the slalom course, the location where the wax is applied prior to the race starting line had largest number of detections and contributed most of the PFAS concentration in both water and soil, with concentrations decreasing as sites were sampled down the ski slope**
- **At the cross-country course, the locations where the wax is applied and then tested prior to the race had the largest number of detections and contributed most of the PFAS concentration in the soil samples, with evidence this contamination is migrating to ponds and a vegetable garden within the racing area.**
- **Non-targeted screening identified more long chain PFAS that aren't typically included in targeted screening including dioic perfluorinated acids, monohydrogen-substituted polyfluoroalkyl carboxylic acids and perfluoroalkyl carboxylic acids.**

References

1. US Environmental Protection Agency. Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS. January 2024.
2. SE Dowd, KL Organtini, J Carlan, FL Dorman. Non-Targeted Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Environmental Samples Related to Alpine Skiing Using Ion Mobility Filtering and High-Resolution Mass Spectrometry. ACS Environ. Au. In publication. 2025

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