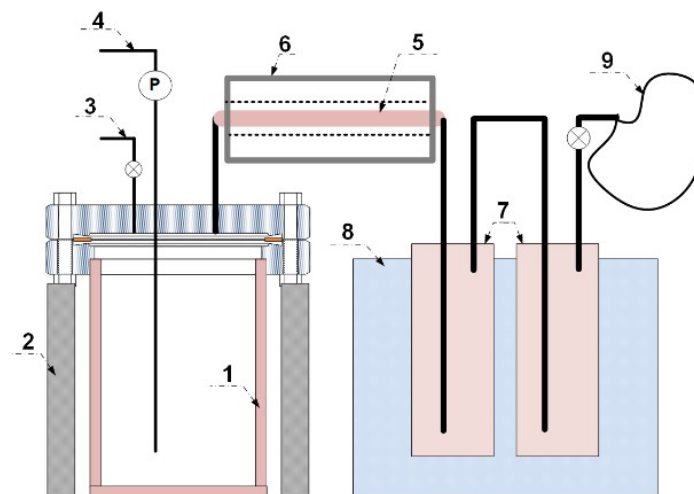


### Electronic Supplementary Information



1. Reactor vessel 2. Radiative heater 3. Gas purge and release system 4. Thermocouple and pressure gauge 5. Transition Tubing 6. Radiative heater 7. Condenser 8. Ice bath 9. Tedlar® bag

**Figure S1.** Experimental setup for batch pyrolysis experiments.

ESI Table S1. Concentrations (µg/kg) of targeted analytes found above detection limit in samples

Sample Name	6:2 Fluorotelomer sulfonic acid (6:2FTS)	8:2 Fluorotelomer sulfonic acid (8:2 FTS)	N-ethyl perfluorooctane sulfonamide ethanol (NEtFOSE)	N-methyl perfluorooctane sulfonamide ethanol (NMeFOSE)	Perfluorobutanoic acid (PFBA)	Perfluorobutanesulfonic acid (PFBS)	Perfluorodecanoic acid (PFDA)	Perfluorodecane sulfonic acid (PFDS)	Perfluorodecanoic acid (PFDoA)	Perfluoroheptanesulfonic acid (PFHpS)	Perfluoroheptanoic acid (PFHpA)	Perfluorooxalanoic acid (PFHxA)	Perfluorooxalanesulfonic acid (PFHxS)	Perfluorononanoic acid (PFNA)	Perfluorononane sulfonic acid (PFNS)	Perfluorooctanoic acid (PFOA)	Perfluorooctanesulfonic acid (PFOS)	Perfluorooctane Sulfonamide (FOSA)	Perfluoropentanoic acid (PFPeA)	Perfluoropentanesulfonic acid (PFPeS)	Perfluorotetradecanoic acid (PFTA)	Perfluoroundecanoic acid (PFUnA)	Sum
Feed-1-Pre	1.06	0.067	0.262	0.382	0.142		0.168	0.092	0.098	0.095	0.039	1.02	0.307	0.082		0.129	1.09	0.059	0.262	0.486	0.034	0.06	5.934
Feed-1-TOP	0.119				5.01	0.214	0.185	0.074	0.108		0.66	2.15	0.052	0.243		0.635	1.3	0.025	5.43		0.046	0.099	16.35
Feed-2-Pre	0.674	0.046	0.172	0.249	0.148		0.112		0.096	0.05	0.07	0.747	0.279	0.066		0.18	0.315	0.035	0.378	0.022	0.037	0.053	3.729
Feed-2-TOP	0.06				3.69	0.108	0.141	0.046	0.076		0.501	1.64	0.037	0.216		0.531	0.84	0.02	3.74		0.033	0.082	11.761
Feed-3-Pre	0.93	0.068	0.225	0.314	0.516	0.046	0.171		0.106	0.081	0.23	1.13	0.308	0.148	0.038	0.206	1.25	0.05	0.833	0.067	0.036	0.069	6.822
Feed-3-TOP	0.06				2.2	0.056	0.098	0.03	0.044		0.358	0.954	0.03	0.14		0.35	0.309	0.02	1.99		0.024	0.055	6.718
650-2-TOP																			0.029				0.029
650-3-TOP																			0.022				0.022
800-1-TOP																			0.02				0.02
800-3-Pre					0.047																		0.047
800-3-TOP																			0.021				0.021

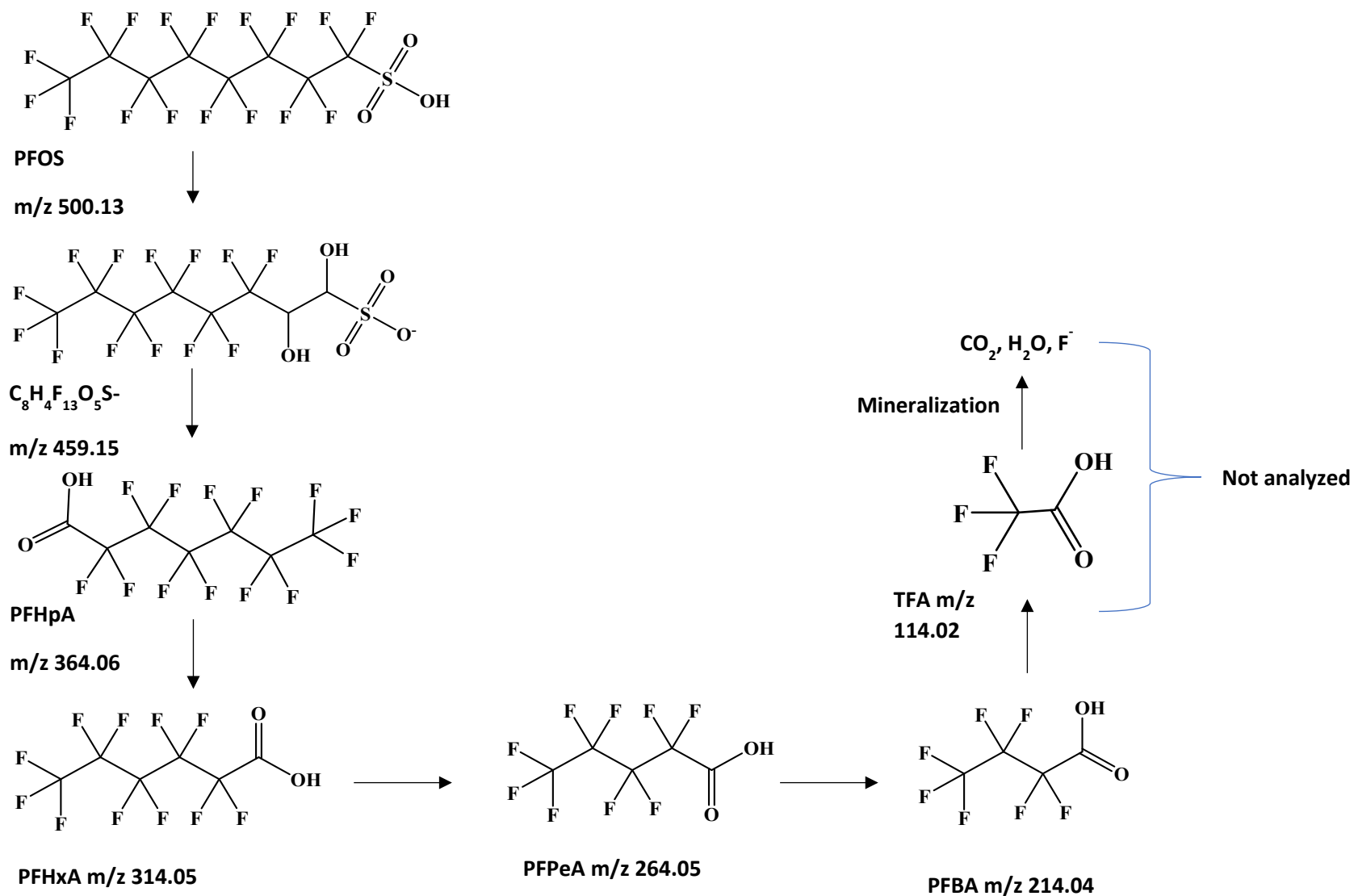
ESI Table S2. Mass (ng) of targeted analytes found above detection limit in samples

Sample Name	6:2 Fluorotelomer sulfonic acid (6:2FTS)	8:2 Fluorotelomer sulfonic acid (8:2 FTS)	N-ethyl perfluorooctane sulfonamide ethanol (NEtFOSE)	N-methyl perfluorooctane sulfonamide ethanol (NMeFOSE)	Perfluorobutanoic acid (PFBA)	Perfluorobutanesulfonic acid (PFBS)	Perfluorodecanoic acid (PFDA)	Perfluorodecane sulfonic acid (PFDS)	Perfluorodecanoic acid (PFDoA)	Perfluoroheptanesulfonic acid (PFHpS)	Perfluoroheptanoic acid (PFHpA)	Perfluorooxalanoic acid (PFHxA)	Perfluorooxalanesulfonic acid (PFHxS)	Perfluorononanoic acid (PFNA)	Perfluorononane sulfonic acid (PFNS)	Perfluorooctanoic acid (PFOA)	Perfluorooctanesulfonic acid (PFOS)	Perfluorooctane Sulfonamide (FOSA)	Perfluoropentanoic acid (PFPeA)	Perfluoropentanesulfonic acid (PFPeS)	Perfluorotetradecanoic acid (PFTA)	Perfluoroundecanoic acid (PFUnA)	Sum
Feed-1-Pre	106.0	6.7	26.2	38.2	14.2	0.0	16.8	9.2	9.8	9.5	3.9	102.0	30.7	8.2	0.0	12.9	109.0	5.9	26.2	48.6	3.4	6.0	593.4
Feed-1-TOP	11.9	0.0	0.0	0.0	501.0	21.4	18.5	7.4	10.8	0.0	66.0	215.0	5.2	24.3	0.0	63.5	130.0	2.5	543.0	0.0	4.6	9.9	1,635.0
Feed-2-Pre	67.4	4.6	17.2	24.9	14.8	0.0	11.2	0.0	9.6	5.0	7.0	74.7	27.9	6.6	0.0	18.0	31.5	3.5	37.8	2.2	3.7	5.3	372.9
Feed-2-TOP	6.0	0.0	0.0	0.0	369.0	10.8	14.1	4.6	7.6	0.0	50.1	164.0	3.7	21.6	0.0	53.1	84.0	2.0	374.0	0.0	3.3	8.2	1,176.1
Feed-3-Pre	93.0	6.8	22.5	31.4	51.6	4.6	17.1	0.0	10.6	8.1	23.0	113.0	30.8	14.8	3.8	20.6	125.0	5.0	83.3	6.7	3.6	6.9	682.2
Feed-3-TOP	6.0	0.0	0.0	0.0	220.0	5.6	9.8	3.0	4.4	0.0	35.8	95.4	3.0	14.0	0.0	35.0	30.9	2.0	199.0	0.0	2.4	5.5	671.8
650-2-TOP																			1.3				1.3
650-3-TOP																			1.0				1.0
800-1-TOP																			0.8				0.8
800-3-Pre					2.2																		
800-3-TOP																			1.0				1.0

**Extracted Internal Standard Recoveries**

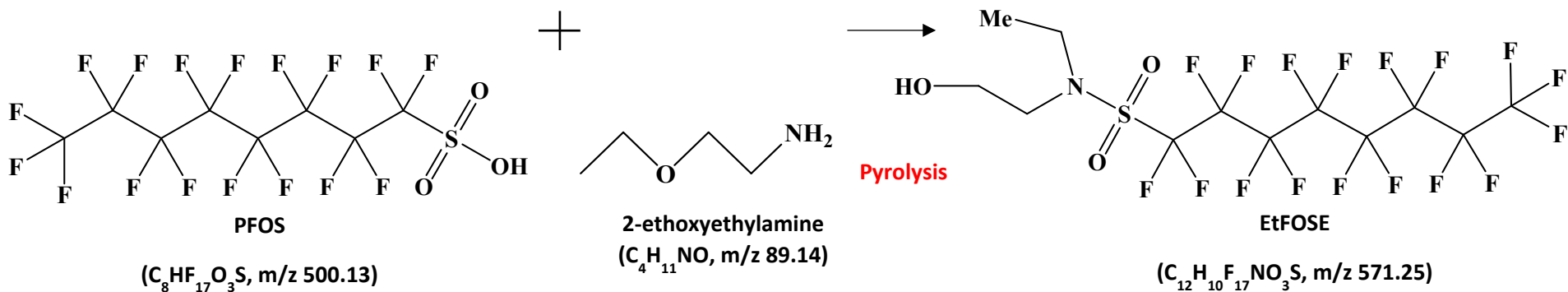
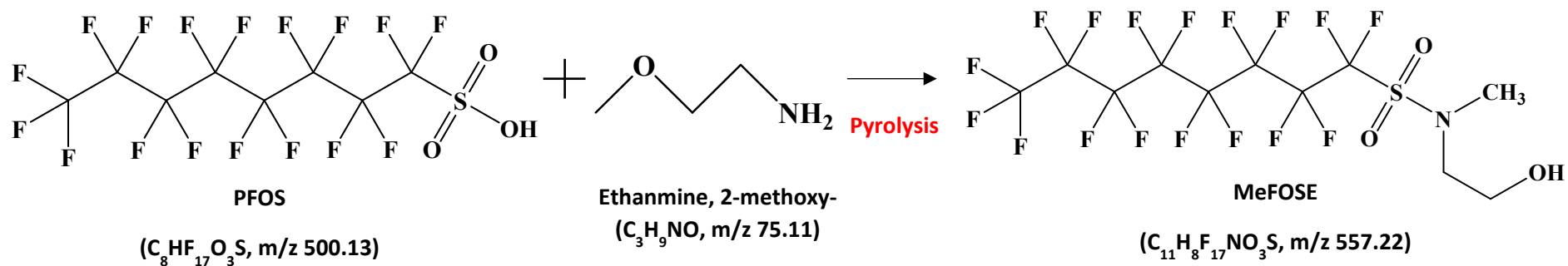
EIS recoveries for the biochar analyses were very good, with 96% of all EIS recoveries falling within the method-developed recovery limits of 50 to 150%. Of the few excursions, the majority were associated with the fluorotelomer sulphonic acids (4:2, 6:2, and 8:2 FTS). In relative terms, EIS recoveries for the py-liquid matrix analyses were not as good as the results for the biochar matrix analyses. This is presumably due to the py-liquid matrix being considerably more chemically complex, with inherent matrix effects likely affecting EIS recoveries. The majority of the excursions for the compounds detected were on the low end of the recovery acceptance range (i.e., <50%); however, no recovery was <20%. These low recoveries, though outside the method-developed recovery limits, were not reduced to the point of causing considerable bias in the accuracy of

the quantitation, as isotope dilution quantitation was employed. Isotope dilution quantitation can be expected to maintain quantitation accuracy when at least 20% EIS recovery is observed; below this level, bias would be expected in target analyte quantitation.



**Figure S2:** Proposed PFOS degradation pathway during pyrolysis. PFBA was detected in the py-liquid; TFA analysis was not conducted in the py-liquid.





**Figure S4:** Proposed PFOS transformation pathway to MeFOSE and EtFOSE during pyrolysis.