Electronic Supplementary Information

Mechanochemical Destruction of Per- and Polyfluoroalkyl Substances in Aqueous Film-Forming Foams and Contaminated Soil

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Supporting Information Summary: 16 Pages, 7 Figures, 6 Tables.

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1. Mechanochemical Milling Programs

AFFF Concentrate. For each milling run, 2.5 mL of Tridol S3 was accurately pipetted onto 25 g of quartz sand, which was also accurately weighed. The ratio of quartz sand to AFFF concentrate was approximately 10:1 w/w. The mixture was placed into a stainless-steel cylindrical milling vessel that had an internal volume of 500 cm^3. Twenty stainless steel balls (15 mm diameter, 13.5 g each) were also placed into the vessel with the AFFF-spiked quartz sand and sealed with a stainless-steel lid. A Retsch PM100 planetary ball mill (Germany) was used for all mechanochemical experiments. The ball mill rotational speed was set to 425 rpm and operated for various time intervals from 15 minutes up to 1440 minutes. A custom milling program was set to switch the direction of the vessel rotation every 15 minutes for the specified time of the trial run to avoid caking on the internal walls of the milling vessel. Interval sampling of the matrix would lead to diminishing the mass held within the stainless-steel vessel, thus altering the internal conditions. Therefore, each data point was generated from a discrete trial run. All experimental runs were conducted under ambient temperature, pressure, and humidity. The initial sample was taken at 15 mins as this timeframe allowed for the homogenization of the Tridol S3 AFFF concentrate and the quartz sand matrix. Reduced MCD conditions (relative to full-scale MCD reactor systems) were selected to follow the degradation of PFASs in Tridol S3 rather than to achieve rapid destruction of the target compounds, thus providing important information related to the mechanism of degradation. As a point of interest, full-scale mechanochemical systems which have the capability to treat persistent organic pollutants and PFASs are typically continuous flow stirred horizontal ball mills.[1–3] These systems create intense ball-to-ball and ball-to-surface collision points, similar to a planetary ball mill, but with significantly more impacts per second due to the larger vessel size (several hundred-liter capacity).

AFFF-Impacted Soil. Approximately 1 kg of the as-received soil was sieved to exclude any particles larger than 2 mm (e.g., rocks, twigs, roots) and subsequently dried at 80°C for 6 hours. No other preprocessing was carried out. For each milling run, 25 g of the dried soil was accurately weighed and placed into a stainless-steel cylindrical milling vessel that had an internal volume of 500 cm^3. 20 stainless steel balls (15 mm diameter, 13.5 g each) were also placed into the vessel with the AFFF impacted soil and sealed with a stainless-steel lid. A Retsch PM100 planetary ball mill (Germany) was used for all mechanochemical experiments. The ball mill rotational speed was set to 425 rpm and operated for various time intervals up to 1440 minutes. A custom milling program was set to switch the direction of the vessel rotation every 15 minutes for the specified time of the trial run to avoid caking on the internal walls of the milling vessel. Interval sampling of the matrix would lead to diminishing the mass held within the stainless-steel vessel, thus altering the internal conditions. Therefore, each data point was generated from a discrete trial run. All experimental runs were conducted under ambient temperature, pressure, and humidity. These reduced MCD conditions were selected to follow the degradation of PFAS in contaminated soil sample rather than to achieve rapid destruction of the target compounds, thus providing important information related to the mechanism of degradation.

2. Analytical Procedures for Targeted (LC-MS/MS)

LC-MS/MS. The extract was analyzed using a Sciex Triple Quad 6500+ LC-MS/MS system running in negative ion mode and using electron spray ionization (ESI). 10 µL of the diluted sample extract was injected into the LC fitted with a Waters C18 analytical column (100 mm x 2.1 mm, 2.5 µm fully porous) and a Phenomenex C18 delay column (50 mm x 2.0 mm, 3 µm) to protect against PFAS originating from within the LC system. The approximate flowrate was 0.5 mL/min to the MS/MS. In line with standard analytical practice, detection was conducted using multiple reaction monitoring mode with two transitions monitored per compound, one as a quantifier and one as a qualifier. A series of eight solvent-based calibration standards were run twice during each analysis batch, prepared at 10, 20, 50, 100, 200, 500, 1000, 2000 ng/L, which also included isotopically labelled internal standards at a fixed concentration. Samples containing an equivalent amount of internal standard were quantified against these. Confirmation of identity was based on retention time and ion ratio matching. Surrogate compounds were added to all samples and blanks to observe the extraction efficiency of the process. Table S1 provides a list of all PFAS analytes that were quantitatively assessed.

3. Extractable Organic Fluorine Analysis

Total organic fluorine (TOF) analysis is a non-selective detection method that utilizes combustion ion chromatography (CIC) and cannot differentiate between organic fluorine and inorganic fluoride.[4] Here, extractable organic fluorine (EOF) analysis was carried out by Eurofins Environmental Testing Australia on both subsets of samples (AFFF-quartz sand; contaminated soil) before and after MCD treatment. The selectivity of the EOF method is directly related to sample preparation and the type of solvent used for extraction. The purpose of EOF analysis was to broadly evaluate the overall presence of both target and non-target PFASs in the untreated and treated solid matrices. In this method, an aqueous methanol solvent was used to extract PFASs from the solid sample material (~0.5 g) and then concentrated to at least 1 mL prior to analysis by CIC. In this work, the EOF results were derived by comparing the concentration in the initial samples versus the concentration in the final samples.

4. LC-MS/MS Target PFAS Analyte List

Table S1. LC-MS/MS PFAS analyte list and definitions.

PFAS Class	Abbreviation	Full Name
Perfluorinated Sulfonic Acids	PFPrS (linear)	Perfluoro-1-propanesulfonic acid
	PFBS (linear)	Perfluoro-1-butanesulfonic acid
	PFPeS (linear)	Perfluoro-1-pentanesulfonic acid
	PFHxS (linear)	Perfluoro-1-hexanesulfonic acid
	PFHxS (mono branched)	Trifluoromethylperfluoropentanesulfonic acid
	PFHxS (di branched)	Di(trifluoromethyl)perfluorobutanesulfonic acid
	PFHxS (Total)	Sum of PFHxS (linear), PFHxS (mono and di branched)
	PFHpS (linear)	Perfluoro-1-heptanesulfonic acid
	PFOS (linear)	Perfluoro-1-octanesulfonic acid
	PFOS (mono branched)	Trifluoromethylperfluoroheptanesulfonic acid
	PFOS (di branched)	Di(trifluoromethyl)perfluorohexanesulfonic acid
	PFOS (Total)	Sum of PFOS (linear), PFOS (mono branched) and PFOS (di branched)
	PFNS (linear)	Perfluoro-1-nonanesulfonic acid
	PFDS (linear)	Perfluoro-1-decanesulfonic acid
Perfluoroalkyl Carboxylic Acids	PFBA	Perfluoro-n-butanoic acid
	PFPeA	Perfluoro-n-pentanoic acid
	PFHxA	Perfluoro-n-hexanoic acid
	PFHpA	Perfluoro-n-heptanoic acid
	PFOA	Perfluoro-n-octanoic acid
	PFNA	Perfluoro-n-nonanoic acid
	PFDA	Perfluoro-n-decanoic acid
	PFUnDA	Perfluoro-n-undecanoic acid
	PFDoDA	Perfluoro-n-dodecanoic acid
	PFTrDA	Perfluoro-n-tridecanoic acid
	PFTeDA	Perfluoro-n-tetradecanoic acid

Perfluorinated Sulfonamides	PFOSA	Perfluoro-1-octanesulfonamide
	N-EtFOSA	N-ethylperfluoro-1-octanesulfonamide
	N-MeFOSA	N-methylperfluoro-1-octansulfonamide
Perfluorinated Sulfonamidoacetic Acids	PFOSAA	Perfluoro-1-octanesulfonamidoacetic acid
	N-EtFOSAA	N-ethylperfluoro-1-octanesulfonamidoacetic acid
	N-MeFOSAA	N-methylperfluoro-1-octanesulfonamidoacetic acid
Perfluoroalkyl Sulfonamidoethanols	N-EtFOSE	2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol
	N-MeFOSE	2-(N-methylperfluoro-1-octanesulfonamido)-ethanol
Fluorotelomer Sulfonates	4:2 FTS	1H,1H,2H,2H-perfluoro-1-hexanesulfonic acid
	6:2 FTS	1H,1H,2H,2H-perfluoro-1-octanesulfonic acid
	8:2 FTS	1H,1H,2H,2H-perfluoro-1-decanesulfonic acid
Other	HFPO-DA	2,3,3,3-Tetrafluoro-2-(heptafluoropropoxy)propanoic acid

5. Tridol S3 AFFF Concentrate General Properties

Table S2. Physical and chemical properties of Tridol S3 AFFF concentrate.

Physical/Chemical Property	Value
Appearance	Clear, pale-yellow liquid
Melting Point	-3°C
Boiling Point	100°C
Solubility with Water	Miscible with water
Density	1.02 g/cm^3
pH	6.5-8

Table S3. Manufacturer's stated composition of Tridol S3 AFFF concentrate (SDS).

Component	CAS Number	Content
Diethylene glycol monobutyl ether	112-34-5	15%-30%
Alkyl dimethylamine oxides	NA	5%-10%
Magnesium sulfate	7489-88-9	1%-5%
Fluorosurfactants	NA	1%-5%
Water	7732-18-5	50%-74%

6. AFFF Concentrate Component PFASs

Table S4. Putatively identified PFAS anions in the Tridol S3 AFFF Concentrate. (Suspect ID derived from NIST PFAS suspect list) Note: QToF equipped with ESI and operated in negative ion mode).

Suspect ID	Compound Type	Putative Formula	Experimental m/z	Expected m/z
3052	FTS	C8H4F13O3S	426.9675	426.9674
3285	FTSAS	C15H17F13NO4S2	586.0217	586.0428
3407	FTSAS Sulfoxide	C15H17F13NO5S2	602.0304	602.0377

7. LC-MS/MS and EOF Degradation Results: Tridol S3 AFFF Concentrate

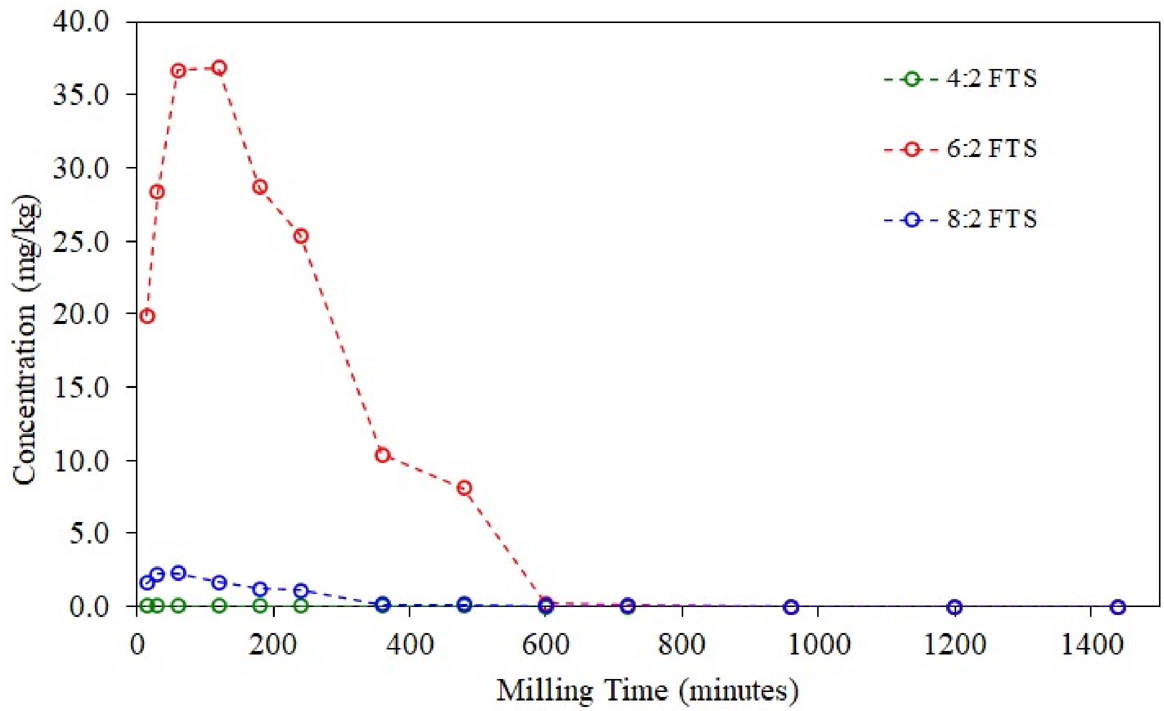


Figure S1. Degradation curves of constituent FTSs in the AFFF-spiked quartz sand.

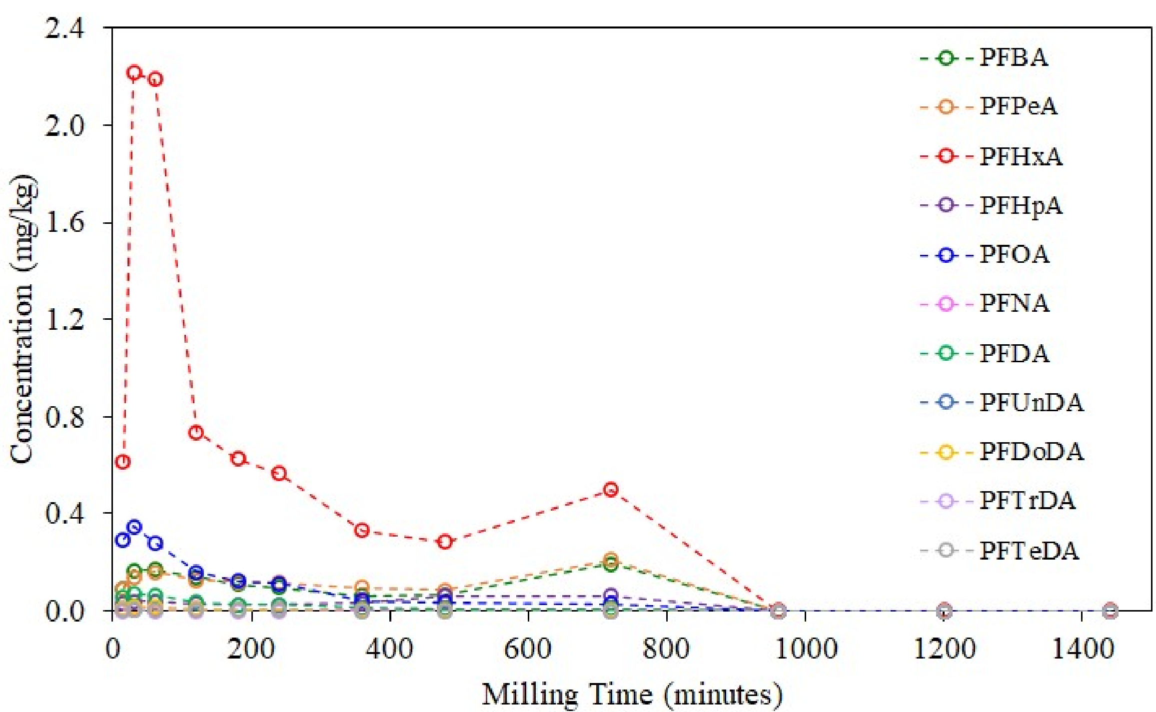


Figure S2. Degradation curves of constituent PFCAs in the AFFF-spiked quartz sand.

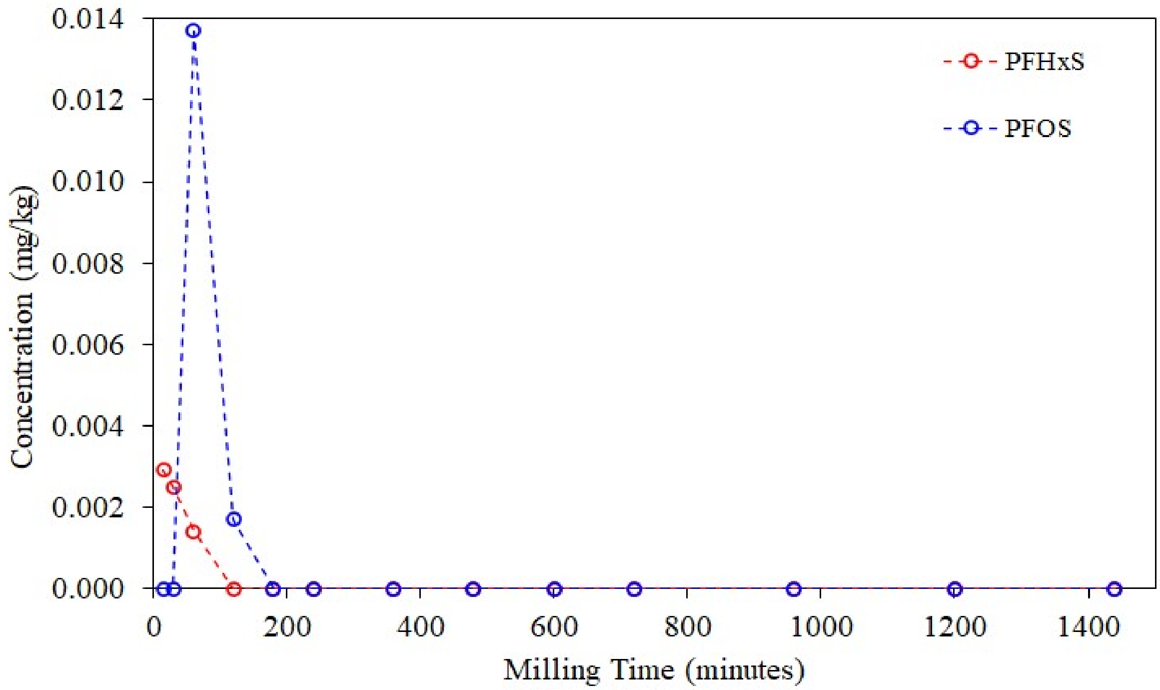


Figure S3. Degradation curves of constituent PFSAs in the AFFF-spiked quartz sand.

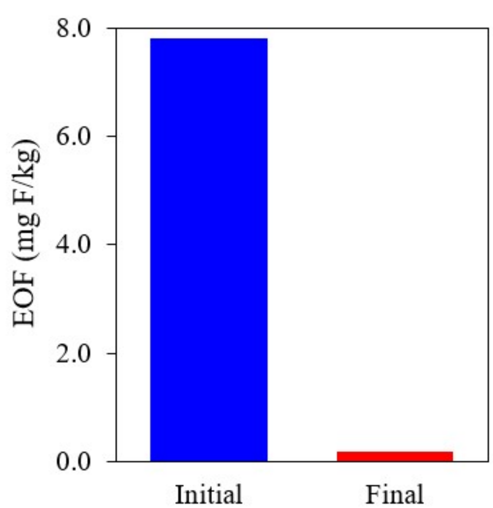


Figure S4. Comparison of EOF for the AFFF concentrate spiked onto quartz sand, before and after MCD. The initial sample was collected at 0 minutes milling time and the final sample was collected at 1,440 minutes milling time.

8. Characterization of AFFF-Impacted Soil

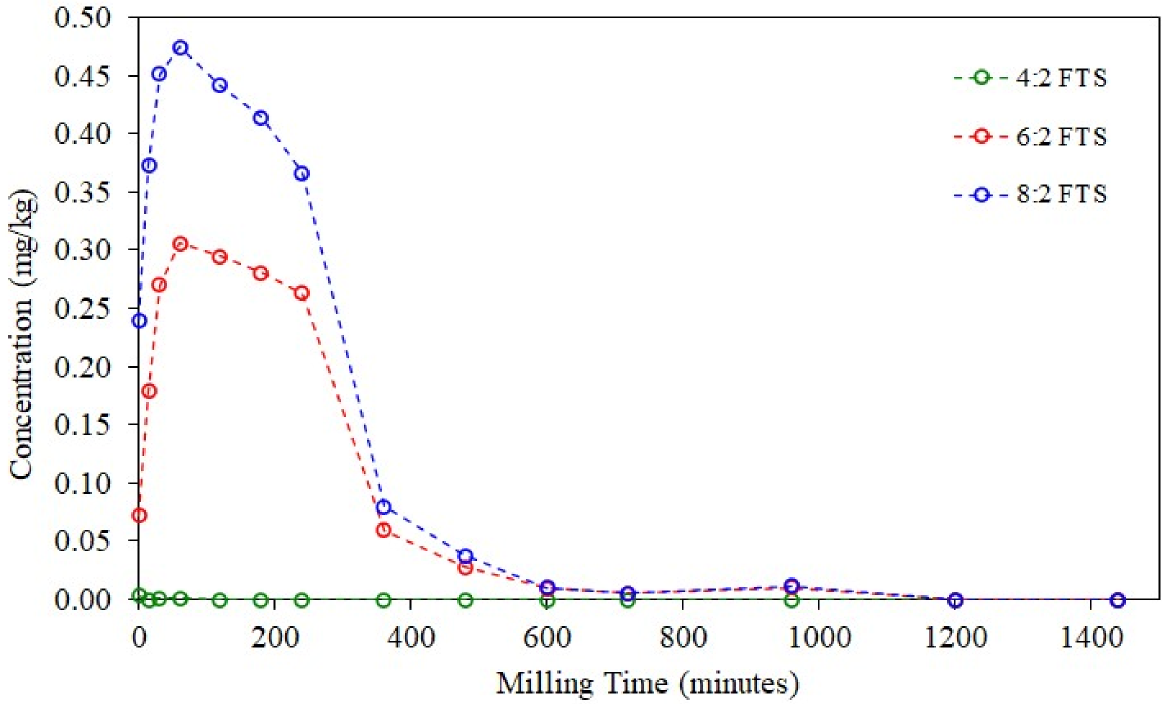
Table S5. Physical and chemical properties of the AFFF-contaminated soil sample.

Physical/Chemical Property	**Value**
Soil pH	5.2
Electrical Conductivity	111 µS/cm
Moisture	19%
Total Organic Carbon	2.3 g/100g dry wt
Organic Matter in Soil	6.9 g/100g dry wt
Ash in Soil	93.1 g/100g dry wt
Specific Surface Area	689.5 m^2/kg

Table S6. PFAS content of AFFF-contaminated soil. Definitions are provided in Table S1.

PFAS Class	PFAS	Value (mg/kg)
Perfluorinated Sulfonic Acids (PFSAs)	PFPrS (linear)	0.0027
	PFBS (linear)	0.0027
	PFPeS (linear)	0.0028
	PFHxS (Total)	0.0039
	PFHpS (linear)	0.0028
	PFOS (Total)	0.0620
	PFNS (linear)	0.0030
	PFDS (linear)	0.0030
Perfluoroalkyl Carboxylic Acids (PFCAs)	PFBA	0.0051
	PFPeA	0.0162
	PFHxA	0.0137
	PFHpA	0.0078
	PFOA	0.0146
	PFNA	0.0231
	PFDA	0.0225
	PFUnDA	0.0107
	PFDoDA	0.0073
	PFTrDA	0.0030
	PFTeDA	0.0030
Perfluorinated Sulfonamides (FASAs)	PFOSA	0.0083
	N-EtFOSA	0.0030
	N-MeFOSA	0.0030
Perfluorinated Sulfonamidoacetic Acids	PFOSAA	0.0030
	N-EtFOSAA	0.0030
	N-MeFOSAA	0.0030
Perfluoroalkyl Sulfonamidoethanols	N-EtFOSE	0.0030

	N-MeFOSE	0.0030
Fluorotelomer Sulfonates (FTSs)	4:2 FTS	0.0030
	6:2 FTS	0.0718
	8:2 FTS	0.2395
Other	HFPO-DA	0.0030



9. LC-MS/MS and EOF Degradation Results: AFFF-Impacted Soil

Figure S5. Degradation curves of constituent FTSs in the AFFF-contaminated soil.

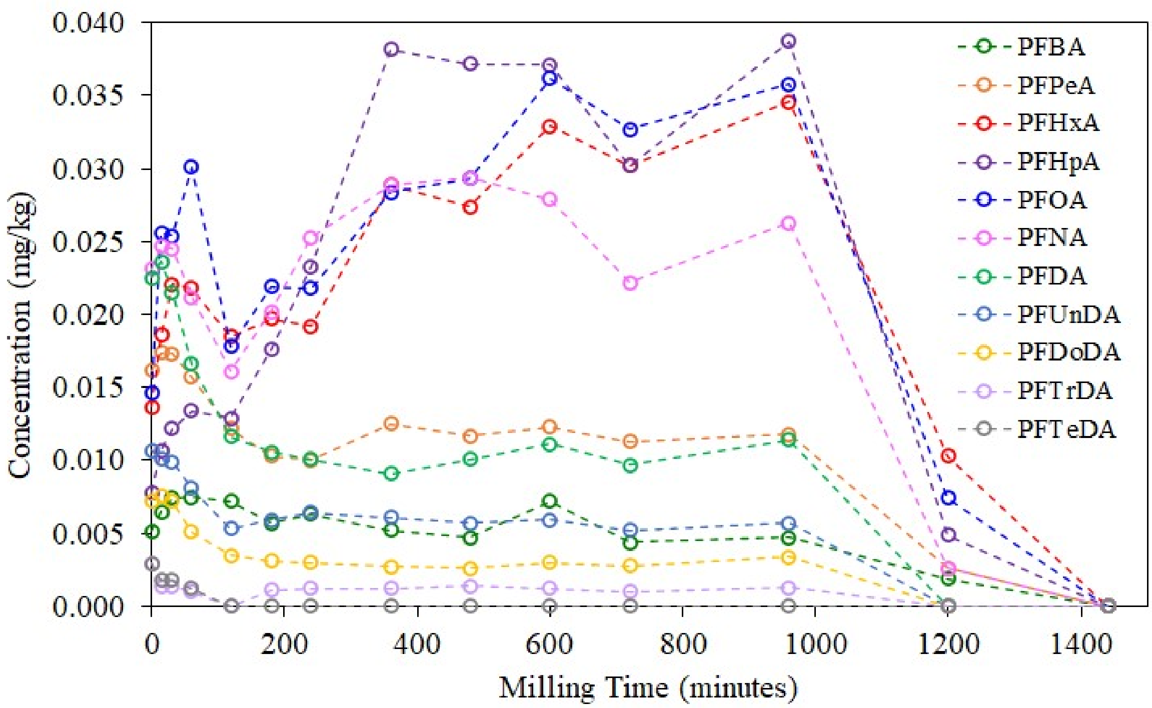
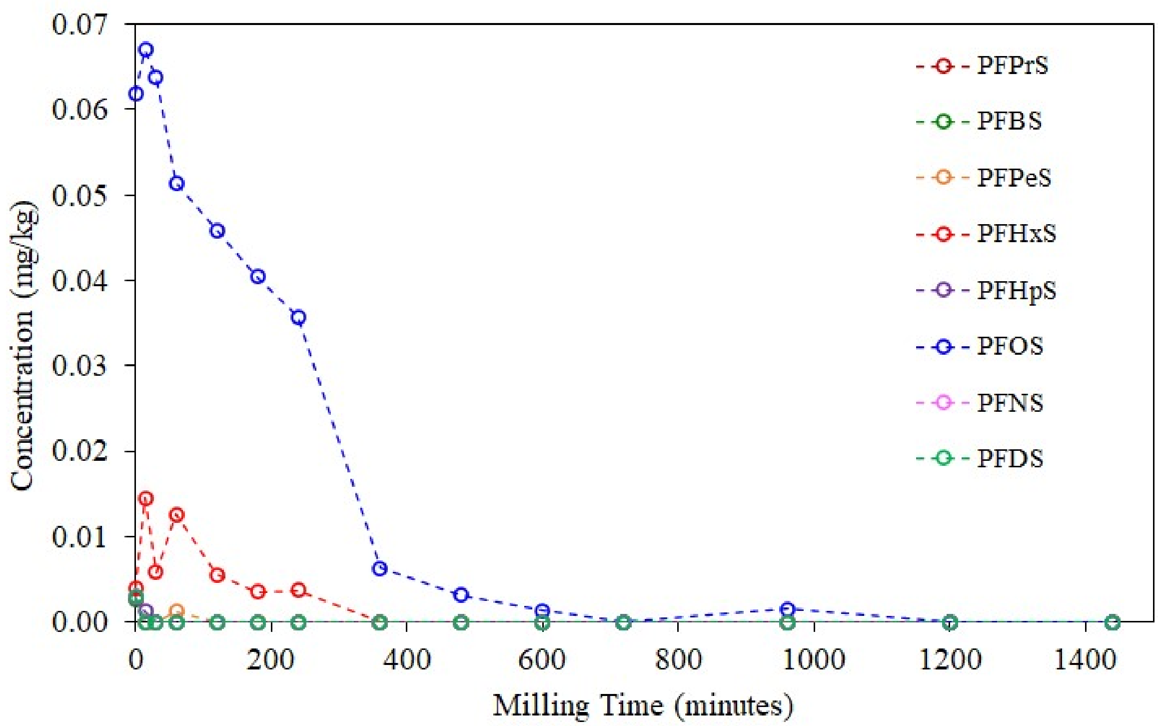


Figure S6. Degradation curves of constituent PFCAs in the AFFF-contaminated soil.



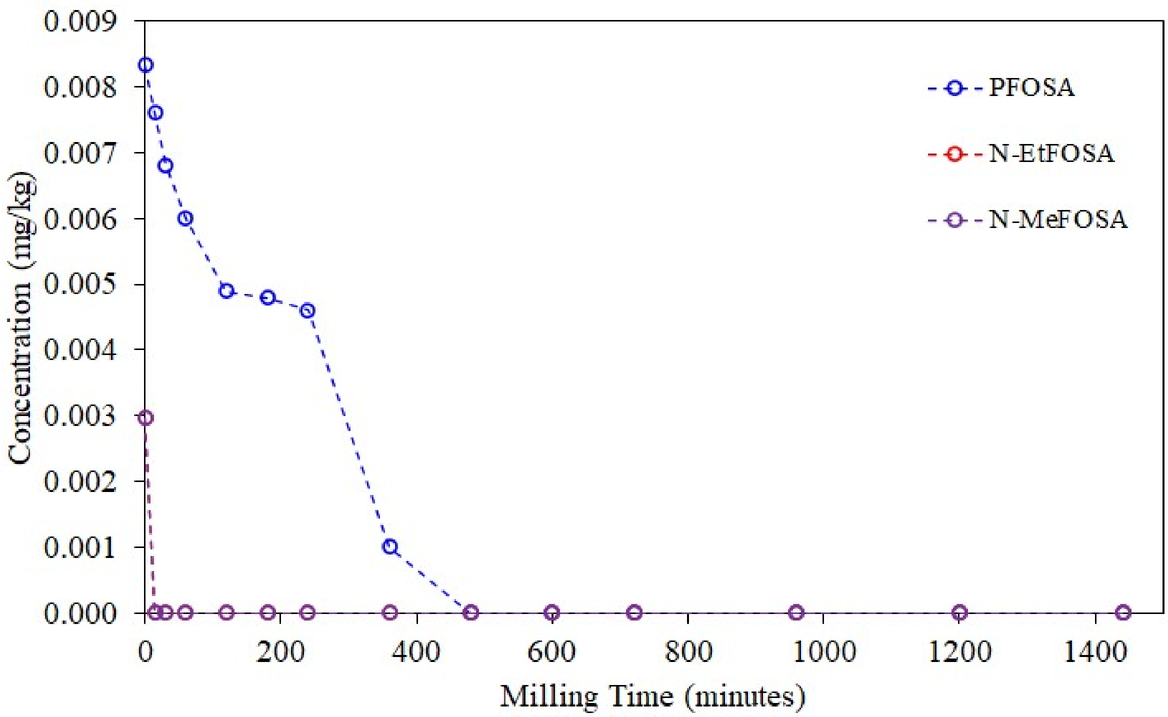


Figure S7. Degradation curves of constituent PFSAs in the AFFF-contaminated soil.

Figure S8. Degradation curves of constituent FASAs in the AFFF-contaminated soil.

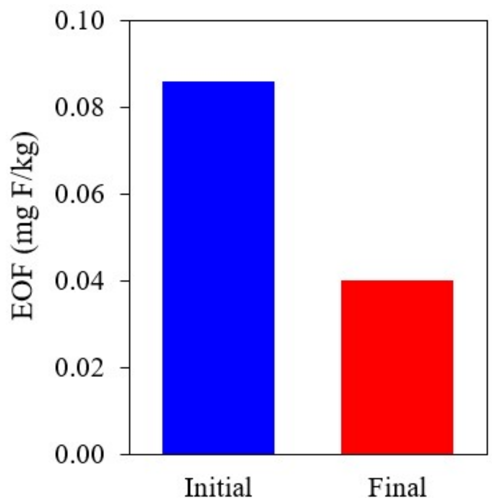


Figure S9. Comparison of EOF for the AFFF-impacted soil, before and after MCD. The initial sample was collected at 0 minutes milling time and the final sample was collected at 1,440 minutes milling time.

References

1 R. J. Cooke, *GEF/UNDP Project on Environmental Remediation of Dioxin Contaminated Hotspots in Vietnam: Independent Expert Evaluation of Three Pilot/Laboratory Scale Technology Demonstrations on Dioxin Contaminated Soil Destruction from the Bien Hoa Airbase in Viet Nam*, Alberta, Canada, 2015.

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